THESIS

ANALYSIS OF PRODUCED WATER FROM THREE HYDRALICALLY FRACTURED WELLS WITH DIFFERENT LEVELS OF RECYCLED WATER

Submitted by

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ABSTRACT

ANALYSIS OF PRODUCED WATER FROM THREE HYDRALICALLY FRACTURED WELLS WITH DIFFERENT LEVELS OF RECYCLED WATER

With the growing use of hydraulic fracturing, injecting large amounts of water into oil and natural gas reservoirs to increase the quantity of oil and natural gas extracted, large amounts of water with low water quality are being created. This water has to be disposed of and many disposal methods have environmental concerns. One method of disposal is treating the water to remove the contaminants that have environmental concerns. Treatment of produced water for reuse, which will be identified as recycled water, as a fracturing fluid is becoming an increasingly important aspect of water management surrounding the unconventional oil and gas industry since the treatment does not have to be as robust as it would for disposal into surface water. Understanding variation in water quality due to fracturing fluid and produced water age are fundamental to choosing a data driven, water management approach. For these reasons, Noble Energy partnered with CSU to analyze the water quality differences between four wells with different levels of recycled water usage in a previous study. In that study, the findings showed a higher organic content of the produced water in the early period due to the presence of emulsified oil. The higher organic content of that produced water was the reason for using recycled water at more wells to determine if the higher organic content was repeatable at a different site. For this study, one well was 100

percent fresh water, another well was one part recycled water and five parts fresh water, and the last well was one part recycled waters and seven parts fresh water.

Based on the data, the inorganic constituents vary more than the organic material. Inorganic variance being greater than organic makes sense due to the fact that the organic matter comes mainly from the fracturing fluid's gel or slickwater component (Sick 2014), despite the organic variance seen in the previous study (White 2014). The inorganic matter mainly comes from the recycled water as seen from the ANOVA testing indicating significant difference between the wells, which is not treated to fresh water levels, and the data from the three wells shows a significantly higher value for the wells fractured with recycled water. A good illustration of the difference in the produced water quality that can be tied to the fracturing water quality is the TDS that was between four and six times higher in the fracturing fluid's base fluid due to the use of recycled water. Of the inorganic constituents measured, aluminum, silicon, zinc, ammonium and sulfate were the only ones that did not show a statistically significant difference between the fresh water well and the recycled wells as indicated by a p value of 0.05 from an ANOVA test. None of the organic constituents showed significant statistical difference between the recycled wells and fresh water well, but they did vary over time indicating that the reactions and interactions with the geological formation affected the wells at a different rate.

The wells did show a statistical difference both between the wells and over time, however, not in the way that was hypothesized as the organic material did not vary based on the wells. Total organic carbon (TOC), dissolved organic carbon (DOC), oil range organics (ORO), diesel range organics (DRO) and gasoline range organics (GRO) all had values 0.367, 0.758,

0.349, 0.768 and 0.707, respectively. The organics showed more significant difference over time with TOC, GRO, and ORO with p-values of 0.005, 0.012, and 0.029, respectively. However, the inorganic data did show significant difference between wells as well as over time. The inorganic constituents boron, barium, bromide, calcium, iron, potassium, magnesium, chlorine, strontium, sodium, and bicarbonate all had p-values of less than 0.01 except for chlorine which was 0.014. Potassium was the only constituent in that list that was not significantly different over time, but silicon and ammonium, which did not differ by well, did show significant difference over time. All of the inorganic constituents were very significantly different over time with no p-value over 0.01. The impact of this on the water management strategies shows that the understanding of the produced water quality and the factors that impact that is still largely unknown. More sampling and testing for well variability based on the ratio of recycled water in the fracturing fluid will allow more data and a better data driven management approach.

ACKNOWLEDGEMENTS

Writing acknowledgements for a thesis is a bit surreal for me. Even now with the end in sight, I look back and wander how I got here. However, it does not take me long to fully appreciate the fact that I would not be here without the help, guidance and support of so many.

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To my other committee members, Drs. Sybil Sharvelle and John Stednick, thank you very much for taking time out of your schedule to sit on my committee. I can only imagine that there are other things you would much rather spend your time on. I hope that I have offered even a nugget of value to you.

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1. INTRODUCTION

Oil and natural gas production has skyrocketed domestically in the US over the last five to ten years despite the current downturn. Much of the growth is due to the expanded use of hydraulic fracturing and horizontal drilling (Ratner and Tiemann 2015), both of which are water intensive with estimated usage of 2.8 million gallons for hydraulic fracturing and if the it is extended hydraulic fracturing with 25 stages, the fracturing is separated into stages fractured individually, uses an estimated 6.5 million gallons (Goodwin 2012). As more wells are fractured in oil and gas fields, the flowback and produced water (produced water), the wastewater coming back to the surface of the well, continues to increase and water management strategies become critically important due to the use of large volumes of water. The Wattenberg Field, in Weld County, CO is currently at the point where the large amount of water that needs to be treated has pushed companies to experiment with different treatment, including recycling the produced water for future fracturing use, and disposal techniques. The treatment currently centers around the removal of solids from the produced water. Clarifiers and coagulant addition are the mechanisms currently used for treatment.

Recycling produced water from wells can help minimize the demand on fresh water in the region. Utilizing recycling would have the benefit of improving a company's public relations profile and still maintain favorable economics. The recycling process requires treatment prior to reuse and can have an effect on the produced water quality. Understanding the differences in produced water quality will be essential in finding a water management strategy.

This study centered on data gathered from a 36-day sampling timeframe. The samples gathered were analyzed for many water quality parameters both at CSU and at an outside EPA-certified laboratory. The goal of the laboratory work was to determine if there was a difference in the produced water from two wells fractured with one part recycled water with seven parts fresh water, which will be labeled Well R1, in one well and five parts fresh water in a second and one fractured only with freshwater in a third, which will be labeled R2.

Chapter 2 of this thesis investigates the literature that might be pertinent to understand prior to examining the data form the three wells. This section combines many references to provide an understanding of conventional and unconventional oil and natural gas extraction techniques, how the industry began fracturing, and why recycling produced water is an important option for producers continuing to use hydraulic fracturing in the future. The chapter ends with clearly defined objectives for the research.

Chapter 3 provides background about the well, including the specifics of the fracturing fluid like TDS. The sampling and analyzing of the sample are described next followed by the results of the analysis. The results not presented in this section of the thesis that support the results discussed are also presented in Appendix B and C.

Chapters 5 provides conclusions that can be made from the results presented in Chapters 3 and 4. Chapter 6 acknowledges certain areas where more research can help provide more data for better understanding of the recycling process. The references used in the thesis are listed in Chapter 7.

2. LITERATURE REVIEW

2.1 The United States and Oil and Gas

The global industrial society and its growth have relied and continue to rely heavily upon oil and natural gas. The extraction of oil and natural gas has gotten more difficult due to the depletion of the more readily available reservoirs. Technological advances in drilling and hydraulic fracturing have allowed unconventional methods of oil and gas extraction to become more attractive financially (Gregory et al. 2011). Unconventional oil and gas plays are locations where the oil and gas has to be extracted from source rock formations that are highly compressed with low porosity like shale formations. As more wells are drilled unconventionally, the technologies that enable unconventional drilling are improving the practicality of unconventional drilling, both technically and financially. In fact, it is currently one of the largest and fastest growing sectors of domestic energy production over the last several years (EIA 2014).

The expansion of the use of unconventional oil and gas extraction, specifically hydraulic fracturing, has improved the forecast for future domestic production and subsequently has reduced the projected amount of crude oil and petroleum products that the US is expected to import. The U.S. EPA Office of Air Quality Planning and Standards agreed with the assumption that the use of unconventional oil and gas wells will continue to grow (OAQPS 2014). Specifically, the total share that imports take up in petroleum products is expected to decrease from 33% in 2013 to 17% in 2040 (EIA 2015). The importance of the petroleum products can be easily seen since they are used for most of the transportation, they supply raw materials for

many products used in the everyday life of Americans and they are heavily involved in electricity generation. Fossil fuels account for 79.3% of primary energy production in the US and 81.5% of total consumption. Currently, natural gas makes up 27%, which is still less than the 39% that is associated with coal usage, of the US energy supply, but is projected to increase over the coming years and eventually become the most leveraged fuel for electricity production in the US, surpassing coal (EIA 2014). Furthermore, the pressure on oil and gas and energy production companies is only expected to increase as global energy demand increases by 37% by the year 2040 (WEO 2014). Domestically, U.S. energy consumption is expected to grow by an average of 0.3% per year through 2040, with the industrial sector having the largest gains at an average of 0.7% per year (EIA 2015).

The projected increase in domestic production is in line with the production increase the domestic producers have seen over the last several years. From 2008 to 2013, the domestic production of crude oil increased from a starting position of 5.0 million barrels per day up to 7.4 million barrels per day, a 48% increase. Over the same time period of 2008 to 2013, natural gas production increased from 20.2 trillion cubic feet per day to 24.3 trillion cubic feet per day, a 17% increase. The increase in natural gas production coincides with an increase in natural gas's share of total U.S. energy consumption rising from 23% to 28%. The trend of increasing production of domestic crude oil and natural gas leads to the prediction of increased production continuing through year 2040 (EIA 2015). The past increases and future increase projections are likely due to the decrease in price associated with higher production.

For crude oil, the increase in production annually until 2040 is projected at 0.9%. For natural gas, the increase for the same time frame is 1.4% per year (EIA 2015). A large part of

this growth in natural gas production will be increases in the development of shale gas reserves. The expectation is for domestic production of shale gas, which includes natural gas from tight geological formations, is to increase from the 11.3 trillion cubic feet produced in 2013 to 19.6 trillion cubic feet in 2040, a 42% increase (EIA 2015). The growth of shale gas production is heavily influenced by the growth in tight gas but federal offshore and onshore Alaska productions are also likely to assist in the growth (EIA 2015).

The figure below, Figure 2-1, shows the plays located through the continental United States (EIA 2015). The plays range from more oil dense areas such as the Bakken, which produces mainly crude oil out of the North Dakota area, to the Marcellus play that mainly produces natural gas in the Appalachian area. The variation in the available hydrocarbons at each play is dependent on the temperatures and pressures of the geological formations (DOW 1977). The differences are important as the areas will have corresponding drilling and operational needs, as well as distinct regulatory requirements, such as the rule in Pennsylvania that does not allow the produced water to be treated in publicly owned treatment works.

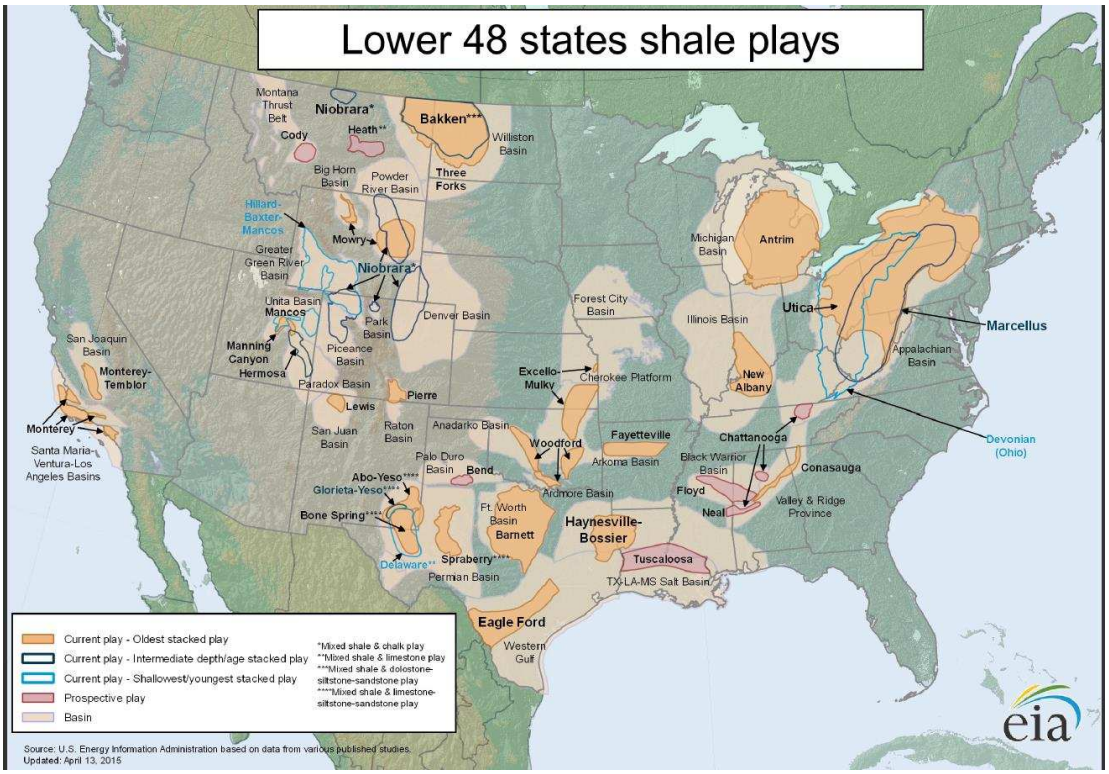


Figure 2-1. The Shale Plays of the Lower 48 States
http://www.eia.gov/oil_gas/rpd/shale_gas.pdf.

2.2 Hydraulic Fracturing

2.2.1 Background

Hydraulic fracturing began in the late 1940s in an attempt, like today, to get more resources out of each well (EPA 2015). At first, the attempts were conducted in traditional vertical wells in conventional oil and gas plays. Conventional oil and gas extraction usually utilizes the drilling of vertical wells into areas that have high permeability, which allows the oil and gas to flow easily up the well to the ground surface for collection. The high permeability areas generally consist of sandstone or carbonate solids, and the pressure differential in the well compared to the surface is enough for the oil and gas to flow freely.

As the oil and gas requirements of industry, as well of the population, have grown, unconventional wells have been explored to meet the demand. The improved technology,

including horizontal drilling, has allowed unconventional plays to be accessed more easily. Combined with the horizontal drilling, hydraulic fracturing has allowed the economical extraction of oil and gas in unconventional fields (EPA 2015). The use of hydraulic fracturing was not heavily utilized in the industry until the technology and demand allowed the companies to produce it economically, which did not occur on a large scale until 2003 (MacRae 2012). The area credited as the first oil and gas play to have economic success with horizontal drilling and hydraulic fracturing, which led the industry to believe in the possibilities of horizontal drilling combined with hydraulic fracturing, was the Barnett Shale area of Texas (Gregory et al. 2011). Hydraulic fracturing and horizontal drilling's popularity grew quickly from that point and some estimates state that 90% of currently producing wells were originally stimulated with hydraulic fracturing techniques (MacRae 2012).

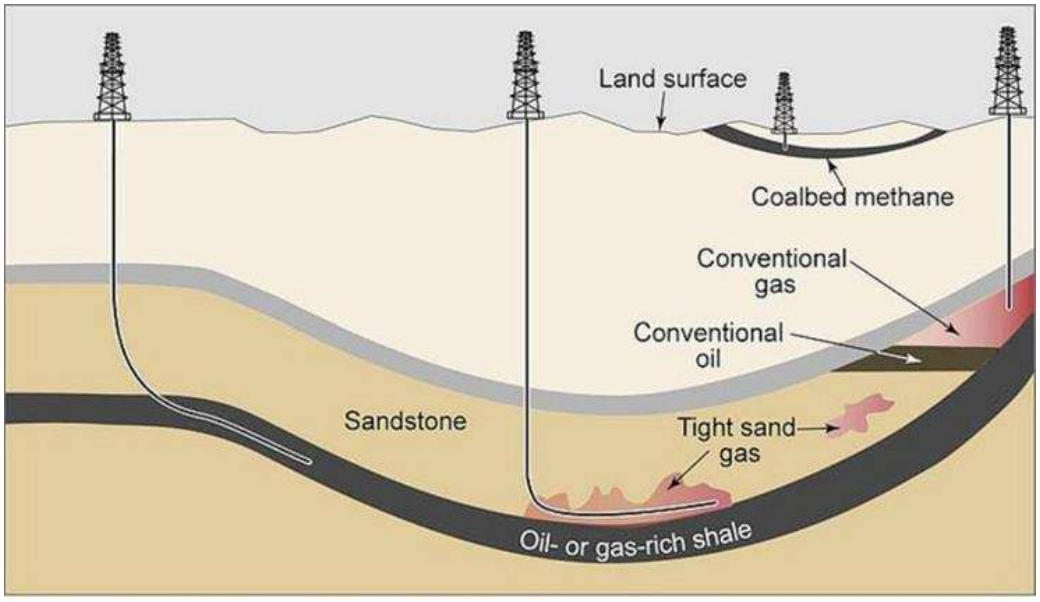
2.2.2 Effects

The effect of fracturing has been tremendous for the United States. The reserve estimates increased by 35% between 2006 and 2009, with the Marcellus Shale production of natural gas via shale formations being a large reason for the increase (Gregory et al. 2011). Hydraulic fracturing, has increased US oil production year over year from 2008 to 2009, the first such increase since 1991. The trend has continued every year since then as well, increasing by 3.2 million barrels per day from January 2008 to May 2014, with 85% of that increase attributed to shale and tight oil formations in Texas and North Dakota (Ratner and Tiemann 2015). 50% of onshore crude oil production is expected to come from hydraulic fracturing by 2019 (EIA 2014). Additionally, energy exports are projected to equal import by 2028 (EIA 2015). Some estimates even have the US becoming the leading oil producer in the world (Ratner and Tiemann 2015).

The estimated increases are due, in large part, to the assumption that the number of oil and gas wells will continue to increase in the coming years (OAQPS 2014).

2.2.3 Extraction

This section will explore and expand on the conventional and horizontal drilling with hydraulic fracturing methods oil and natural gas collection. Figure 2-2 gives a visual representation of the differences between conventional and unconventional oil and gas production (Gregory et al. 2011). Both methods are harvesting the hydrocarbons from geological strata where plant and animal organic matter was deposited and converted over time into the hydrocarbons (EPA 2004).



Sources: U.S. Energy Information Administration and U.S. Geological Survey.

Figure 2-2. Conventional and Horizontal Well Oil and Gas Production

In this study, the Niobrara formation is the one being harvested. The Niobrara is a formation in the Wattenberg Field. The wells in the Wattenberg Field average a depth of 7600-8400 (Smith, Holman et al. 1978). The Wattenberg Field is estimated to have roughly 5.2 trillion cubic feet of natural gas, most of which can only be extracted through hydraulic fracturing

techniques (Dhanasekar 2013). Figure 2-3 shows a cross-section of the Wattenberg field and the depth of the Niobrara.

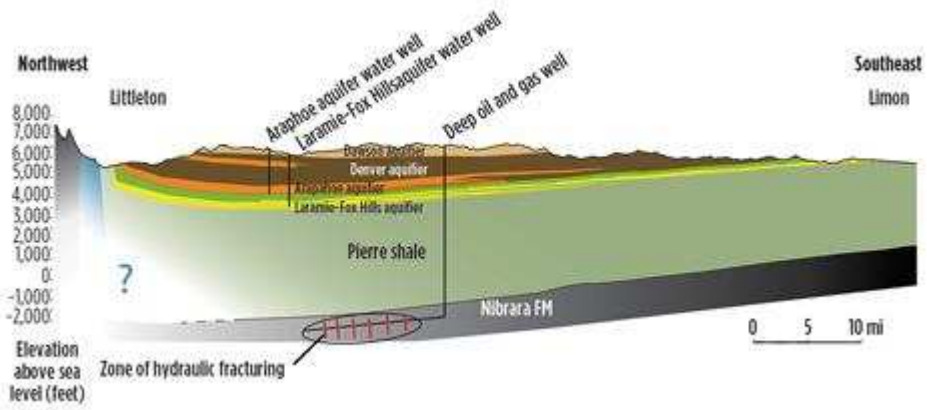


Figure 2-3. Cross-section of the Wattenberg Field (http://www.freerepublic.com/focus/f-news/3094221/posts)

2.2.3.1 Conventional

As stated previously, conventional oil and gas wells typically utilize vertical wells that tap into geological areas that freely release the stored hydrocarbons based on the pressure differential from the formations to the ground surface. The reservoirs that conventional wells tap into usually have high permeability with the oil and gas trapped by a geological formation. This formation prohibits the fluid from leaving the source rock and allows for accessibility for harvesting the hydrocarbons (Schenk and Pollastro 2002). The permeability is what allows the extraction of the oil and/or gas to leave the source rock. If the permeability is not high enough, then the well must be stimulated to increase the permeability and allow for economical extraction of the hydrocarbons. In terms of water usage, 80 percent of the total water required for conventional production is consumed in secondary recovery, which uses methods like water injection to increase pressure in the reservoir, and that number represented 70 percent of onshore oil production in 2005 (Wu and Chiu 2011). The simplicity of conventional methods is what allows conventional oil and gas recovery to be economical despite its low output of oil

and natural gas compared to hydraulic fracturing, but it is also what limits the potential reserves.

2.2.3.2 Unconventional

The source rock for unconventional oil and gas reservoirs has a lower permeability, and the pressure differential is insufficient to liberate the hydrocarbons for surface flow. Therefore, the formation must be stimulated. The stimulation in hydraulic fracturing creates fissures and cracks that increase the permeability of the source rock. Shale is a common source rock that contains hydrocarbons. Shale is fine-grained and primarily composed of clay minerals and other particles that are similar in size to silt (Gregory et al. 2011). As shown in Figure 2-2, fracturing is utilized primarily with horizontal drilling since horizontal wells can replace many traditional vertical wells, adding additional economic benefits of reducing drilling costs (Arthur 2008). Hydraulic fracturing utilizes high pressures and large amounts of water, therefore, it is vital that production companies have access to enough water to meet their needs (Gregory et al., 2011). Approximately two to seven million gallons of water were required for each well (Ranm, 2011; Stephenson, 2011; Lee, 2011; Nicot, 2012; Suarez, 2012; Goodwin, 2013; Hickenbottom 2013). The contact length of the well, combined with the hydraulic fracturing is what allows producers to extract the resource economically (Gregory et al. 2011). Hydraulic fracturing and horizontal drilling is economically viable despite the high cost associated with pumping fracturing fluid, which is engineered specifically for each well, and acquisition, which includes trucking and other costs, and usage of the water and other fracturing fluid additives due to higher oil and gas production per well (Wu and Chiu 2011). Additionally, hydraulic

fracturing with horizontal drilling uses less drilling overall and thus each well, despite the higher cost per well, can have a better return on investment (Gregory et al. 2011; Fitzgerald 2013).

2.2.3.3 Fracturing Fluid Characteristics

Hydraulic fracturing fluid is engineered specifically to maximize the extraction potential of the well. The fluid is composed of many components, as shown in Table 2-1 (DOE 2009). However, despite the complexity of the mixture for the fracturing fluid, the majority of the mixture, 99.5%, is water and sand, or some other granular proppant used in place of sand (EPA 2004; FracFocus 2015). The water acts as the carrier fluid that transports the other chemicals needed to maintain the higher permeability created in the geologic formation, typically shale or other tight formations, and is used to create the pressure to fracture the strata initially. The sand or other proppants keep the fractures open so the pressure does not reclose the fractures, maintaining the permeability of the formation (FracFocus 2015). Once the proppant is in place to maintain the initial fractures, the hydrocarbon fluids can freely flow from the source rock up to the well-head (Kuafman 2008).

Table 2-1. Typical Fracturing Fluid Components
http://energy.gov/sites/prod/files/2013/03/f0/ShaleGasPrimer_Online_4-2009.pdf

EXHIBIT 36: FRACTURING FLUID ADDITIVES, MAIN COMPOUNDS, AND COMMON USES.

Additive Type	Main Compound(s)	Purpose	Common Use of Main Compound
Diluted Acid (15%)	Hydrochloric acid or muriatic acid	Help dissolve minerals and initiate cracks in the rock	Swimming pool chemical and cleaner
Biocide	Glutaraldehyde	Eliminates bacteria in the water that produce corrosive byproducts	Disinfectant; sterilize medical and dental equipment
Breaker	Ammonium persulfate	Allows a delayed break down of the gel polymer chains	Bleaching agent in detergent and hair cosmetics, manufacture of household plastics
Corrosion Inhibitor	N,n-dimethyl formamide	Prevents the corrosion of the pipe	Used in pharmaceuticals, acrylic fibers, plastics
Crosslinker	Borate salts	Maintains fluid viscosity as temperature increases	Laundry detergents, hand soaps, and cosmetics
Friction Reducer	Polyacrylamide	Minimizes friction between the fluid and the pipe	Water treatment, soil conditioner
	Mineral oil		Make-up remover, laxatives, and candy
Gel	Guar gum or hydroxyethyl cellulose	Thickens the water in order to suspend the sand	Cosmetics, toothpaste, sauces, baked goods, ice cream
Iron Control	Citric acid	Prevents precipitation of metal oxides	Food additive, flavoring in food and beverages; Lemon Juice ~7% Citric Acid
KCl	Potassium chloride	Creates a brine carrier fluid	Low sodium table salt substitute
Oxygen Scavenger	Ammonium bisulfite	Removes oxygen from the water to protect the pipe from corrosion	Cosmetics, food and beverage processing, water treatment
pH Adjusting Agent	Sodium or potassium carbonate	Maintains the effectiveness of other components, such as crosslinkers	Washing soda, detergents, soap, water softener, glass and ceramics
Proppant	Silica, quartz sand	Allows the fractures to remain open so the gas can escape	Drinking water filtration, play sand, concrete, brick mortar
Scale Inhibitor	Ethylene glycol	Prevents scale deposits in the pipe	Automotive antifreeze, household cleansers, and de-icing agent
Surfactant	Isopropanol	Used to increase the viscosity of the fracture fluid	Glass cleaner, antiperspirant, and hair color

Note: The specific compounds used in a given fracturing operation will vary depending on company preference, source water quality and site-specific characteristics of the target formation. The compounds shown above are representative of the major compounds used in hydraulic fracturing of gas shales.

Fracturing fluids can be divided into two types: slickwater or gel-based, with gel based fracturing being either linear or cross-linked. The difference is based on the amount of polymer added to the mixture, which can greatly increase the viscosity of the fluid. Slickwater fluids

have a low viscosity and therefore can transport only small proppants and require high pressure head pumps. Gel based fluids have a higher viscosity and larger proppants, but require lower head pumps to move fluid down well-bore, with crosslinked gels having the higher viscosity of the two gel based fluids (Fracline 2012).

The rest of the chemicals added to the mixture are chosen based on the characteristics of the source rock. The chemical additives may include clay control agents, friction reducers, acid, corrosion inhibitors, scale inhibitors, biocides, surfactants, gelling agents, cross-linkers, buffers and breakers among others. These properties are used for aiding fluid dissolving properties, proppant transport, well-bore integrity maintenance and formation permeability maintenance (FracFocus: Chem Use 2015). Whichever fracturing fluid is used in the stimulation, the goal is to form fissures in as much source rock as possible, then keep those fissures open for extraction (Kaufman 2008).

2.2.3.4 Water Usage

The difference in water usage for the two oil and gas extraction techniques is based on the amount of pressure needed to release the oil and gas in unconventional wells. For conventional drilling, the main water use is for drilling the well. The use can increase due to the need for flooding the reservoir for additional oil and gas extraction (Gregory et al. 2011). Water use per well is greater in horizontal wells utilizing hydraulic fracturing than in conventional well design, but the amount of water used per BTU produced is lower (Goodwin and Carlson et al. 2013). The lower water demand per unit energy produced in unconventional production also corresponds to lower wastewater produced per unit energy (Lutz et al. 2013). With the lower water usage and wastewater production per unit energy to the lower surface footprint due to

less wells required, leads to the argument that unconventional production is more environmentally sustainable, if the well is properly constructed to prevent groundwater contamination.

The water footprint argument for gas extraction can also be applied across all energy production techniques. As Figure 2-3 points out, natural gas extraction and transport requires less overall water usage than any other fuel extraction and processing (Mielke et al. 2010).

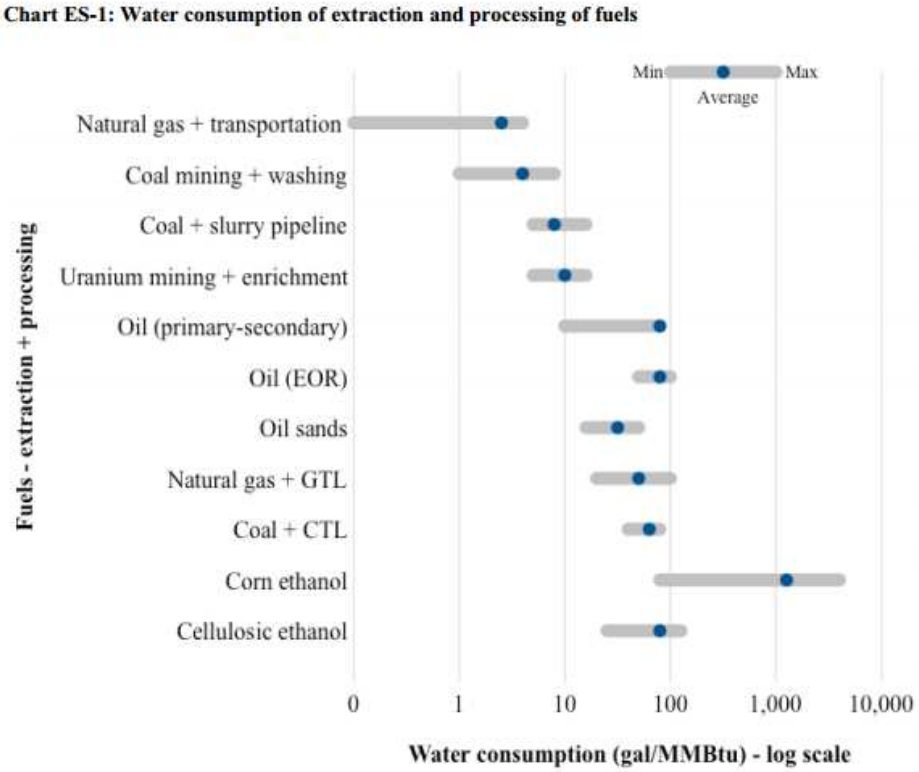


Figure 2-4. Water Usage for Extraction and Processing of Energy Fuels
http://belfercenter.ksg.harvard.edu/files/ETIP-DP-2010-15-final-4.pdf.

2.2.4 Contentious Nature of Hydraulic Fracturing

The economic benefit of oil and gas extraction, particularly with the expanded use of unconventional methods, competes with the desire to protect the environment. With the potential for more domestic manufacturing and energy savings, politicians and industry

lobbyists will not allow environmentalists to prohibit hydraulic fracturing in the near future. Despite the high likelihood that anti-fracturing groups will not be able to stop fracturing from continuing, the need for innovations in the handling and treatment of the operations before, during and after the initial stimulation will be critical items to address going forward.

2.2.4.1 Environmental Issues

Gregory (2011) stated the environmental implications succinctly in his report noting that one of the challenges will be maintaining the economic feasibility of production while being responsible for the natural resources and public health that could be effected by oil and gas operations. Maintaining the environment and public health is an important issue due to the rapid expansion of tight oil and shale gas using hydraulic fracturing, especially considering the potential impacts on United States drinking water, both ground and surface, as well as potential impacts on air quality (Ratner and Tiemann 2015). This issue was pressed further into the spotlight by the recent publication from the EPA that groundwater is susceptible to contamination from hydraulic fracturing activities (EPA 2015). However, concerned parties regularly point out the fact that in 2005, fracturing was specifically exempt from the regulations under the Safe Drinking Water Act (MacRae 2012). Whether drinking water impacts are rare or not, or environmental regulations apply or do not, the concern is justified with 25,000 to 30,000 new wells being drilled between 2011 and 2014 (EPA 2015).

2.2.4.1.1 Air Emissions

Air pollution associated with hydraulic fracturing operations has also gained attention as operations have expanded. The emissions can be created in many of the stages of production

and include pad, road and pipeline construction, well drilling and completion, produced water collection and processing, and all phases of refinement, storage and transportation. The main air pollutants of concern are methane, volatile organic carbons (VOC), nitrogen oxides (NOx), sulfur dioxide, particulate matter (PM) and various others (Ratner and Tiemann 2015 and EPA 2012). These emissions can react with nitrogen oxides in the air and form ozone. Fort Collins consistently has a low rating from the State of the Air Report and received an F, with 8.6 more high ozone days from 2009 (SOTA 2015). This increase in Fort Collins could be caused by several factors, which includes the increase in fracking in Weld County and other places along the front range.

2.2.4.1.2 Trucking

Trucking is a large issue for societal and environmental concerns. Transporting the millions of gallons of water needed for fracturing each well can require roughly 1,500 truck trips (Boulder County Research 2013 and NTC 2011). The impact of the constant flow of trucks is felt especially harshly in communities with heavy oil and gas extraction, i.e. many wells located in a small geographic area. The truck traffic also affects roadways, as the heavy weight of the trucks at scale could add usage for which the roadway was not designed. The damage could then result in repair costs and construction traffic delays. Accident rates are also higher, noted as increasing between 15 and 65 percent, in areas with hydraulic fracturing activity, and fatalities and major injuries also increased (Graham et al. 2015). The specific air emissions of concern for trucking are VOC, carbon monoxide, NOx and PM, 2.5 and 10 (EPA 2008).

2.2.4.1.3 Land issues

Land issues are similar to trucking issues in societal and environmental concerns. The increase in wells and, therefore, well pads have caused the operations to become closer to land owners, communities and waterways. The counter argument is that hydraulic fracturing reduces the amount of well pads overall, a fact supported by many sources including Colorado Oil and Gas Association (Arthur et al. 2008). However, despite the reduced well pad quantity, roughly 9.4 million people lived within a mile of a hydraulically fractured well between the years of 2000 and 2013, roughly 3 percent of the US population. Additionally, that mile radius around all the hydraulically fractured wells nationwide includes 6,800 drinking water sources that provide water for over 8.5 million people (EPA 2015).

2.2.4.1.4 Water Issues

With the proximity of the wells to the population and the water sources on which they rely, the concern over water safety is well founded. Concerns for groundwater contamination include the development of the well, the drilling through aquifers and the casing surrounding the well bore, cementing and the completion of the well (Ratner and Teimann 2015). The new EPA study on hydraulic fracturing risks to drinking water offers a more detailed explanation of how hydraulic fracturing might impact drinking water (EPA 2015). In the study, the authors note that cement casing is a critically important feature for protecting aquifers that are drilled through. The casing, if extended below the bottom of the aquifer, reduces the risk of groundwater contamination by a factor of 1000. The study furthers explores the potential risk to ground water through hydraulic fracturing based on depth of the source rock below the aquifer. In places, like the Denver-Julesberg basin in Weld County, where the source rock is

several thousand feet below the aquifer, the likelihood of a fracture travelling through the overlying rock to the drinking well is low (EPA 2015). However, the likelihood of impact increases as the source rock approaches the ground surface and aquifers. Potential impacts increase further when wells are located near each other or near older or abandoned wells. The proximity of fractured wells could cause intermingling of the fractures created by the multiple wells. Old and abandoned wells are susceptible due to their design or other reasons, like outdated well plugs. The potential contaminations or "frac hits", as they are referred to in the study, suggest that intermingling could affect the well components and result in fluids released at the surface (EPA 2015). The surface impacts can extend beyond well components failing. Transporting of produced water usually involves truck traffic and, as noted previously that traffic accidents increase in fracturing areas, spills can occur. Spills, in reported sites in Pennsylvania and Colorado, were recorded between 0.4 and 12.2 per 100 wells, with 74% of those being caused by failing containers (EPA 2015). Spills that migrate to water bodies can impact the water quality, which is the cause for the concern.

2.3 Water Management and Treatment

With the potential for environmental damage, specifically to water sources, the oil and gas industry will have to develop practices that mitigate and manage the impacts they might cause on the surrounding area. This fact is especially pertinent in regards to the companies' water management strategies. These water management strategies are developed for several reasons. In some cases, like Pennsylvania, water management is required by regulatory agencies. However, in many cases, the water management strategies are developed in response to stimuli resulting from costs. The costs associated with water in hydraulic fracturing

oil and gas production are; sourcing the water used for the fracturing process and treating produced water. Both the water acquisition and wastewater production require transportation and the wastewater also requires treatment (Ratner and Tiemann 2015).

If one tries to calculate the initial water needs for the well, assuming 5 million gallons of water used for stimulating each well, and based on the EPA estimate of 30,000 wells fractured from 2011 to 2014, then the water needed for fracturing was 150 billion gallons. The sheer volume of water requires a high degree of coordination for water gathering and delivery to the well site, as well as treatment and disposal. The usage, though a small percentage of the overall water usage in the United States, does add to the problem of water scarcity in regions, especially regions considered to be in high or extremely high water stress. From January 1, 2011 through May 31, 2013, 48 percent of wells were in high or extreme water stress and 56 percent of wells were in drought regions, including 100 percent of the wells in the Denver-Julesburg basin (Freyman 2014).

Wastewater volume, though lower than the volume used to fracture the wells, also requires attention. Estimates for oil and gas wastewater production in the United States was 15 to 20 billion barrels per year in 2009, and that number is sure to have risen with the increase in wells (Clark 2009). Flowback, which typically lasts from one to four weeks after initial flow, accounts for up to 40 percent of total water that is removed from the well (Arthur 2008). Flowback fluids have properties similar to the fracking fluid that was used to stimulate the well. As the well matures, the wastewater becomes less like the fracturing fluid and more of a reaction between the fracturing fluid and the geologic formation of the source rock and then is termed produced water. Produced water is generally lower than the amount of water injected into the well, but

Barnett Shale is an exception with the produced water equaling or even exceeding the injected volume (EPA 2015). Either way, all this wastewater from unconventional wells requires treatment and/or disposal.

2.3.1 Disposal

As the industry has evolved, including during the time dominated by conventional drilling, companies have experimented with many different methods for disposal. The volume of wastewater produced creates pressure for the industry to find ways to treat and dispose of the water in means that are cost effective, and regulatory agencies have attempted to maintain the effectiveness of the treatment to minimize risks to the public and environment. In Colorado, produced water is disposed of by three means: underground injection wells (60 percent), evaporation ponds and discharge to surface water (20 percent for each) (COGA 2011).

2.3.1.2 Publicly Owned Treatment Works (POTWs)

The use of POTWs is an option for disposal of wastewater; however, there are many constraints that limit the use of this method of produced water disposal. The first limitation can be the cost. POTWs charge a fee for cleaning the water they receive to pay for operations and maintenance. However, an even larger limitation is regulations that the POTWs face from the EPA and state agencies. The main concerns with treating produced water are total dissolved solids (TDS), oil and grease (Gregory et al. 2011).

2.3.1.2 Evaporation Ponds

Evaporation pond usage, as noted previously, accounts for 20 percent of the produced water disposal in Colorado. The method utilizes, as the name indicates, evaporation of the

water so that the contaminants are left in the pond. The usage of evaporation ponds is only sustainable if the inflow (produced water and precipitation) is less than the evaporation rate, which is dependent upon pond size and depth and can be hindered by solids and chemical levels. Another concern is the attractiveness of the water bodies to birds and other animals, which would be covered by oil and grease if they land in the pond (NETL Fact Sheet). A final concern is the air emissions associated with ponds, such as volatile organic compounds (VOCs) like benzene, toluene, ethylbenzene and xylenes among other volatiles(O&G Journal 2009; EPA 2009).

2.3.1.3 Reverse Osmosis

Reverse osmosis is a process of utilizing a pressure gradient through a membrane that is semi-porous allowing water to diffuse through while partially rejecting salts and organic molecules. The pressure gradient separates the water from the contaminant by the filter by allowing the water particles to pass through while capturing the contaminants behind the filter. The concentration of the contaminant left behind in the membrane must be disposed of properly. The contaminants that can be removed include organic molecules and salt ions and RO is commonly employed in desalination processes (Xu 2006). The water produced from this membrane separation technique is of high quality; however, the process is very energy intensive. Any process that is energy intensive will require high operating costs, unless the energy is cheap to produce, and the cost makes this particular treatment technique economically unfeasible with current technology (Cline 2009).

2.3.1.4 Thermal Distillation and Crystallization

Thermal distillation requires evaporation, just like the evaporation ponds, to treat the produced water and separate the water from the dissolved contaminants. Once the water is evaporated, a heat exchanger condenses the vapor to produce purified water. It has been shown that distillation can remove up to 99.5 percent of dissolved solids with the potential to reduce disposal costs (ALL Consulting 2003). Thermal distillation has the ability to treat produced water with a TDS up to 125,000 mg/L of TDS. However, this technology is like reverse osmosis in that it is more expensive than disposing through deep underground injection and purchasing fresh water for future fracturing (Veil 2008).

2.3.1.5 Deep Underground Injection

Deep underground injection has become the most popular method for disposing of produced water (Clark 2009). Injection wells are used most often due to the cost of disposal being the lowest, however, that cost can increase due to distance to the wells' sites. Additional constraints on disposal wells are regulations that ban them in several states. The regulations stem from reports that show the potential for aquifer contamination as well as the potential to induce seismic activity (Dores 2012). When the method is utilized for disposal, the disposal occurs in a Class II disposal well (Veil 2004).

2.3.1.6 Beneficial Reuse

Beneficial reuse is another method that oil and gas producers use to dispose of produced water. This method involves treating the produced water through various treatment techniques prior to subsequent usage in industrial applications, crop or tree irrigation, wildlife

habitat enhancement and on fields for livestock. The advantage of beneficial reuse is the ability to have a lower standard of treatment as opposed to disposing to a surface water body. The main concern for water quality is TDS, specifically for sodium, chloride, calcium, magnesium, iron, barium, boron and strontium (Nijhawan 2006).

2.3.2 Recycling

Another form of beneficial reuse is recycling treated produced water to be used in the hydraulic fracturing process of a new well. The process of treating the water for reuse can be much simpler than treating it for disposal or other forms of beneficial reuse. This is due to the fact that TDS in the produced water can be beneficial for the next well stimulation. However, high TDS negatively affects fracturing additives like cross-linkers. The use of recycled water seems to be occurring due to pressure from society or regulations. For instance, in Pennsylvania, the concerns from citizens and environmental groups and the effects of produced water in rivers pushed the Pennsylvania Department of Environmental Protection to issue an order for POTWs to stop accepting produced water. The order, which specifically targeted TDS effluent to be less than 500 mg/L, along with a geology in the region of the hydraulic fracturing that was not conducive to injection wells prompted companies to become more creative with their produced water treatment. One company responded to the inability to use POTWs by recycling more than 95 percent of its produced water for fracking additional wells (Rassenfoss 2011). And for the industry as a whole, the reuse rates in the Marcellus region have jumped to 90 percent (Charneske 2015).

2.3.2.1 Drawbacks

The reuse of produced water for future fracturing fluid presents some difficulties. Bacterial growth and chloride contamination both present safety concerns that producers must be cognizant of when exposing their employees to the produced water (Vidic 2010). The bacteria could also be a concern for well-bore integrity, as bacteria can foul a well if it grows in the well. As discussed previously, the difficulties arise due to chemical reactions. Specifically, the level of TDS affects the effectiveness of emulsion friction reducers. The effectiveness of the friction reducers is negatively affected because the high concentration of divalent cations in the produced water hinders the ability of the friction reducers to invert (Sareen et al. 2014 and Zhou et al. 2014). The reduction in effectiveness has caused fracturing companies to experiment with new chemistry.

2.3.2.2 Benefits

Reusing produced water in fracturing future wells has multiple benefits including societal, environmental and economic. The societal benefits include showcasing a company's commitment to protecting communities and the communities' resources. If done strategically, recycling minimizes truck traffic and reduces the strain on water sources in the region. As noted previously, minimizing strain on fresh water is important especially considering the location of most of the wells in water scarce regions. One economic impact of recycling produced water is shown by a study by Zhou et al. (2014) in which they measured the effectiveness of a new friction reducer on a well site in Texas. The friction reducer was tested with recycled water with a TDS value of 250,000 mg/L and 50,000 mg/L hardness. The results showed better pumping and pressure rates at the surface (Zhou et al. 2014).

2.4 Research Purpose and Objective

As unconventional oil and gas plays become more popular, the increase in wells will have a two-fold impact on any region's water resources. The increase in hydraulic fracturing will add to demand for fresh water sources and treatment solutions for produced water. It is with these two concerns in mind that companies need to seriously consider recycling produced water for fracturing future wells. For the Wattenberg area, companies need to begin gathering data on the effects of recycling produced water in fracturing. Gathering the data on the differences of using fresh water versus recycled water will become important when companies determine produced water treatment strategies.

Little work has been done to understand how different base fluids affect the quality and quantity of produced water. However, The Colorado State University Center for Energy Water Sustainability conducted research on fresh water versus recycled wells in Weld County with two recycled wells and two fresh water wells (White 2014). The recycled well, a seven part fresh water to one part recycled water, and fresh wells had significantly more samples than the secondary wells. Figure 2-4 shows the difference in the fracturing fluid used, the vertical depth and the base water volume of the different fracturing packages used for the wells at Crow Creek, the previous study, and Chandler State, the current study.

Table 2-2. Crow Creek Wells Compared to Chandler State Wells (White 2014)

Designation	Well Name	API #	True Vertical Depth (ft)	Base Water Volume (gal)	RecycleWater Vol. (gal)	Stages	FracFluid Package
Primary Recycled (7:1)	Crow Creek State **AC36-73HN**	05-123-37423-00-00	6685	2,371,163	296,395		PermStim
Primary Fresh	Crow Creek State **AC36-76-1HN**	05-123-37420-00-00	6742	1,335,328	0		PermStim
Secondary Fresh	Crow Creek State **AC36-73-1HN**	05-123-37422-00-00	6747	2,403,381	0		PermStim
Secondary Recycled (5:1)	Crow Creek State **AD31-79HN**	05-123-37426-00-00	6674	2,301,153	383,526		PermStim
Primary Fresh	Chandler State **D15-72-1HN**	05-123-38322-00	6834	3,390,198	0	23	SilverStim
Primary Recycled (7:1)	Chandler State **D15-73-1HN**	05-123-38323-00	6759	3,677,478	459,684	23	SilverStim
Primary Recycled (5:1)	Chandler State **D15 74-1HN**	05-123-383321-00	6840	3,154,662	525,777	23	SilverStim

The depths are all similar as is the formation that the wells were targeting. The main difference is the Fluid Package, PermStim versus SilverStim. According to Halliburton's website, Permstim is a polymer as is SilverStim. Figure 2-5 shows the spatial difference between the two wells, which is approximately 50 miles. Figure 2-6 shows the Wattenberg Field in the Denver Julesburg Basin as well as the formations of interest for the oil and gas companies in the area.

Figure 2-5. Map Showing Location Between Crow Creek and Chandler State (Google Maps)

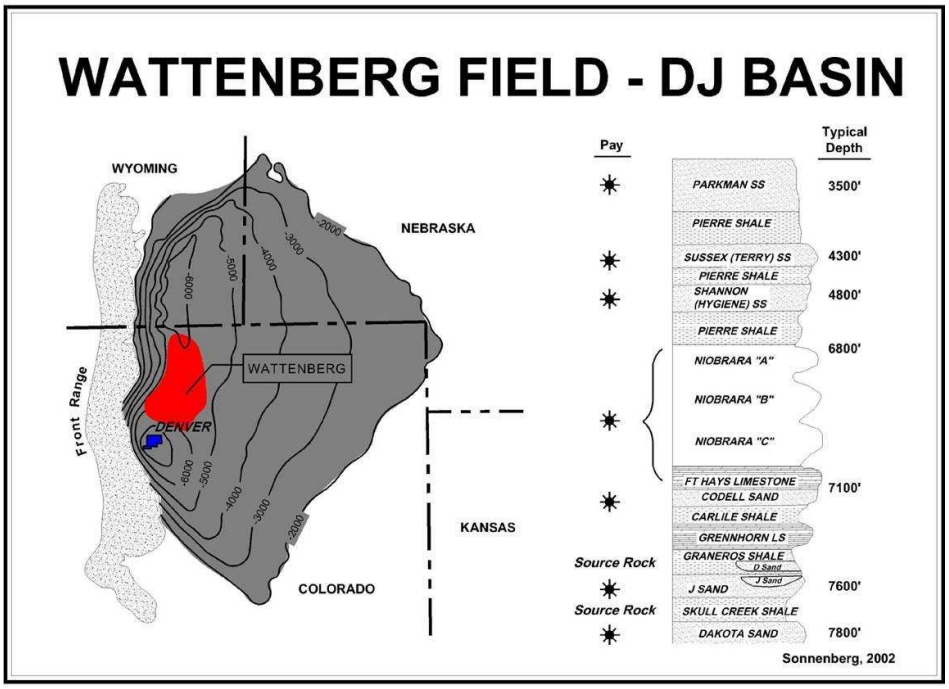


Figure 2-6. Wattenberg Field in the DJ Basin and the Geologic Formation http://www.syrginfo.com/operations/operations-overview.

The Crow Creek data from the sampling showed that the recycled wells had higher early TOC and turbidity values than the fresh water wells, which is shown in Figure 2-7 and 2-8, respectively.

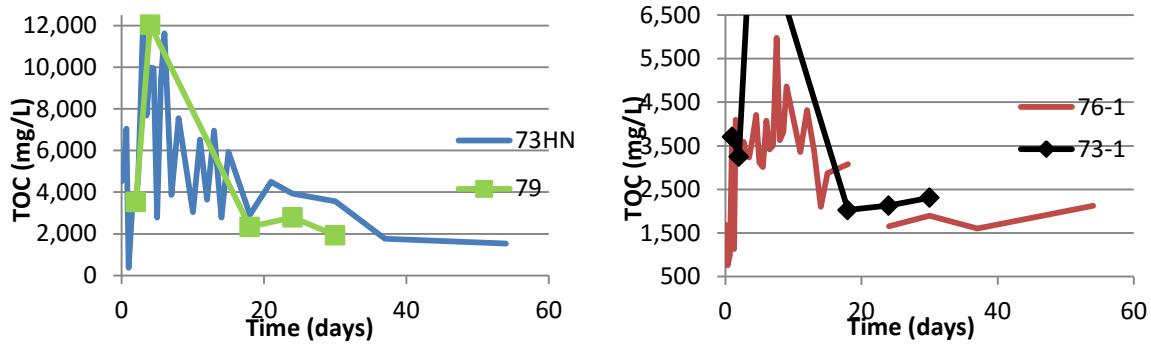


Figure 2-7. TOC Comparison (White 2014)

73HN and 79 are the two recycled wells. Well 79 was used as a check of the data and only has 5 days of sampling, but does appear to verify the results found in Well 73HN. The same sampling method was used for 76-1 and 73-1. Looking at wells 73HN and 76-1, the TOC value is higher in the early sampling period in the recycled well.

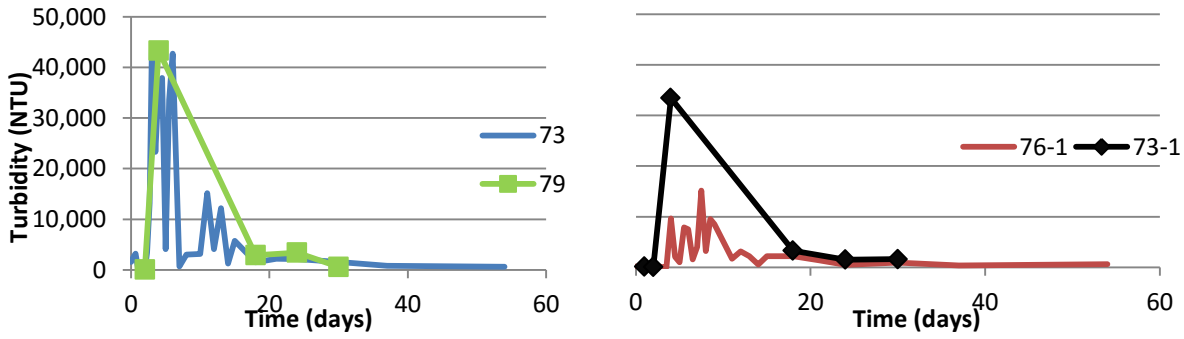


Figure 2-8. Tubidity Comparison

Similar to the data from the TOC measurements, the turbidity is higher in the recycled well in the first 14 days. The TOC of the recycled well's produced water remains twice as large as the fresh water well's produced water through day 30 with values of 3,568 and 1,869, respectively. By day 40, the fresh water well's TOC is 2,123 and the recycled water well's TOC is

1,526 indicating that the impact of the recycled well does not last throughout the sampling. Both also appear to be become similar near day 20 around with turbidi. This difference in the early period of the sampling led to the belief that the recycled base fluid impacts the produced water quality, especially the organic difference.

The wells studied in this thesis were chosen by Noble to verify the data found in the Crow Creek Wells. The purpose of this research is to utilize laboratory methods to measure the organic and inorganic content and LCMS data to analyze produced water samples to gain a better understanding of the difference between the recycled and fresh water base fracturing fluids. The objectives of this research were:

- Collect produced water samples from three wells in the Wattenberg field. The three wells will allow us to compare differing levels of recycling in hydraulic fracturing fluids. The first well will use all fresh water, the second will use 1:5 recycled/fresh water and the last will have 1:7 recycled/fresh water.
- Perform laboratory methods, both in house and through a state certified analytical laboratory, to measure different organic, inorganic and LCMS data from the samples collected to measure if there are temporal differences in the samples.
- Utilize laboratory techniques to analyze the samples to better understand how the different fracturing fluids affect the quality of the produced water.

3 WATER QUALITY CHARACTERIZATION

3.1 Introduction and Purpose

Analysis of produced water quality from wells fractured with recycled water has not been analyzed to any great degree and then compared to wells fractured with fresh water. Understanding of the effects of recycled water may impact treatment strategies should a difference be found between produced water quality in fresh and recycled wells. This is especially important for oil and gas companies whose current water management strategy, like the operators in the Wattenberg field, has been developed for fresh water wells.

The objective of this study was to measure the water quality from the three wells based on organic and inorganic constituent characterization to answer several questions about the possible differences caused by using recycled water in the fracturing fluid. The questions analyzed are the following:

- Is there a statistical difference in organic constituents found in the produced waters?
- Is there a statistical difference in inorganic constituents found in the produced waters?
- Do the organic and inorganic constituents in the produced water change temporally?
- What effect might the potential differences have on water management strategy?

3.2 Fracturing Fluid

Table 3-1 displays data gathered from FracFocus.org about the composition of the fracturing fluid. The table shows the similarities of the fracturing fluid make up. The largest difference in the ingredients is friction reducer, breaker, buffer and cross-linkers. These substances only make a small portion of the overall fluid by percent mass. However, our

research group has shown that small changes in the fracturing fluid can have large effects on the water chemistry of the produced water (Sick 2014).

Table 3-1. Fracturing Fluid Composition As Found On FracFocus.org

Purpose	Trade Name	Ingredients	Well F Max Conc. (% by Mass)	Well R1 Max Conc. (% by Mass)	Well R2 Max Conc. (% by Mass)
Base Fluid	Fresh Water	Fresh Water	85.5	76.4	N/A
Base Fluid	Recycled Water	Recycled Water	0	10	N/A
Proppant	Sand - Premium White	Crystalline silica, quartz	13.6	12.7	13.86
Gelling Agent	WG-18 Gelling Agent	Guar gum derivative	0.2	0.2	0.1
Breaker	Vicon NF Breaker	Sodium chloride	0.1	0.1	0.03
		Chlorous acid, sodium salt	0.03	0.03	0.1
Buffer	BA-40L Buffering Agent	Potassium carbonate	0.06	0.1	0.04
		Isopropanol	0.04	0.03	0.01
Surfactant	OilPerm FMM-2	Citrus, extract	0.01	0.1	0.02
Crosslinker	CL-37 Crosslinker	Triethanolamine zirconate	0.02	0.02	0.01
		Glycerine	0.005	0.005	0.01
		Propanol	0.005	0.005	0.01
Additive	Cla-Web	Ammonia Salt	0.01	0.01	0.01
Activator	CAT-3 ACTIVATOR	EDTA/Copper Chelate	0.009	0.009	0.01
Crosslinker	CAT-3 CROSSLINKER	Zirconium, acetate lactate oxo ammonium complexes	0.005	0.005	0.01
		Ammonium Chloride	0.003	0.003	0.01
Friction Reduction	FR - 66	Hydrotreated light petroleum distillate	0.004	0.007	0.002
Activator	CAT - 4	Diethylenetriamine	0.003	0.003	0.003

The difference in the friction reducer can be explained by the use of recycled water. Recycled water has a higher TDS, which can minimize the effectiveness of friction reducers due to the divalent cation content of the recycled water. Table 3-2 displays the TDS data from the three fracturing fluids. For Well R1, the data corresponds to the theory that the friction reduction would be affected as they had to use nearly double the amount of friction reducer as the Well F, but it does not follow for Well R2 where half the friction reducer was required than Well F despite a much higher TDS.

Table 3-2. Total Dissolved Solids in Fracturing fluids

Total Dissolved Solids in Fracturing Fluid						
	Well F		Well R1		Well R2	
	Fresh	Recycled	Fresh	Recycled	Fresh	Recycled
TDS (mg/L)	1445	n/a	1305	30389	870	23521
Gallons (MG)	3.39	0	3.22	0.46	2.63	0.53
Total Gal	3.39		3.68		3.16	
Total TDS (mg/L)	1445		8001		6233	

In this study, the fracturing fluid is anticipated to be the largest contributor to the quality of the produced water due to the age of the well during the sampling period. Typically, the water coming out of a well will have more similarities to the fracturing fluid early in the well's life cycle and will shift over time to be a combination of the fracturing fluid and any compounds and elements that might have interacted with the fluid. However, the fracturing fluids influence on the water coming out of the well can last for weeks after the fracturing process is complete and the well is already producing.

3.3 Sample Collection

Nineteen samples were collected at the Chandler State well site over a 36-day period. The sampling began the first day of oil and gas production and was gathered directly from the well-head, which is a potential reason why the day one data shows discrepancy. The rest of the samples, which occurred every day for the first 14 days, then every three days until day 29 with the final sample taken on day 36, were taken from permanent separators, which separate much of the oil from the water coming out of the well. Each well has its own separator, which allowed for measuring each individual well. For work performed in the CSU laboratory, a one liter bottle was filled for sample testing, including the pH which was taken at the well site, as well as 2 volatile organic analysis (VOA) glass vials for liquid chromatography mass

spectrometry (LC-MS) testing. For eAnalytics, a 250 mL container and two additional VOAs were filled. The VOAs were all filled so that there was no air space when the cap was placed on the VOA.

3.4 Methods

3.4.1 Analysis Performed at CSU

The following tests were performed at Colorado State University.

3.4.1.1 Gravimetric Solids Analysis and Turbidity

Solids were measured using gravimetric solids analysis and turbidity. Gravimetric solids analysis was utilized to determine the TS, TSS, TDS, TVS, VDS, VSS and the tests were performed in accordance with Standard Methods, Method 2540. All the tests utilized weighing to measure the solids. For TS, a sample is weighed and put into the oven at 105 degC for drying and is reweighed after drying. For TSS, a sample is poured over a Whatman 934-AH 1.5-um-equivalent pore size glass microfiber filter. The filter is then placed in the 105 degC oven for drying. The TDS sample is collected from the collected water after filtering. It is also placed in the 105 degC oven for drying. For the volatile testing, the same procedures are followed for TS, TSS and TDS but the samples are placed in the 550 degC oven to mineralize the organics and can be used to estimate the organic loading in the produced water. Turbidity, which is a measure for colloidal solids that have a strong impact on light reflection, was measured using a HACH 2100 N turbidimeter. The device reads the light refraction in nephelometric turbidity units (NTUs). Measuring the turbidity was performed in accordance with HACH Method 8000.

3.4.1.2 TOC and DOC

TOC and DOC were both analyzed using a Shimadzu TOC-VCSH analyzer. This analyzer determines the TOC by finding the difference between total carbon and total inorganic carbon. The two amounts are measured when carbon in the sample is oxidized to CO_2. For TOC, the sample is taken directly from the well samples, then diluted at a ratio of one (1) to 10. For the DOC, the same process for TDS and VDS is utilized and the sample for DOC is gathered after filtering through a 1.5-um-equivalent Whatman 934-AH glass microfiber filter.

3.4.1.3 pH , Alkalinity, Carbohydrates

pH was measured on site using HACH probes using CDC401. For alkalinity, Standard Methods 2320B was used for measurement. The Carbohydrate method is described in detail in Appendix D.

3.4.1.4 LC-MS

Testing the samples using LC-MS was performed less frequently than the other samples in this study. The sample days chosen for LC-MS testing was days 1, 2, 6, 10, 14, and 20. The test uses Agilent 1290 series liquid chromatography with Agilent 6530 quadrapole time of flight (QTOF) that has Electrospray Ionization of positive and negative modes. 12 L/min was provided for shear gas flow with a temperature of 400 degC. The nebulizer pressure was 30 psig. The regular gas flow was also 12 L/min but with a temperature of 325 degC. The voltages were 750, 60, 120 and 500 V for the octopole RF peak voltage, skimmer voltage, fragmentor voltage, nozzle voltage, respectively. The mobile phases were 0.1% formic acid in water for A, 0.1% formic acid in acetonitrile for B. The gradient, which was run for 18 minutes at 30 degC, was

95-80% of A for 1-8 minutes, 80-5% of A for 8-17 minutes and 5-95% of A for 17-18 minutes. Mobile phase B makes up the remaining portion of the fluid in the gradient.

Due to the limit of chemical standards, the qualitative analysis of the organic compounds was performed by searching the library in Agilent Technology Software based on the exact mass of the chemicals used for hydraulic fracturing in U.S (Chemicals Used in Hydraulic Fracturing 2011). A 5 ppm mass accuracy was applied for detection of chemical compounds.

3.4.2 Analysis Performed by eAnalytics

eAnalytics is the lab outside of CSU that was contracted to perform several tests on the samples. The tests included determining the content of metals, ammonia (NH_4), bicarbonate (HCO_3), bromide (Br), chloride (Cl), sulfate (SO_4), gasoline range organics (GRO), diesel range organics (DRO), oil range organics (ORO), total petroleum hydrocarbons (TPH) and benzene, toluene, ethylbenzene, and xylenes (BTEX). The method for determining the metals, aluminum (Al), boron (B), barium (Ba), bromine (Br), calcium (Ca), iron (Fe), potassium (K), magnesium (Mg), sodium (Na), silicon (Si), strontium (Sr), zinc (Zn), chlorine (Cl), was EPA 6010C that involves adjusting the pH to below 2 and using inductively coupled plasma-atomic emission spectrometry (ICP-AES). Ammonia was determined using EPA 350.1. Bicarbonate determination used EPA 310.1. Bromide's method was EPA 300 .0. Chloride's method was EPA 9253. Sulfate utilized ASTM D516. GRO, DRO, ORO used EPA methods 8260C, 8015, and 8015 respectively. TPH was a summation of GRO, DRO, and ORO. BTEX method was EPA 8260C.

3.4.3 Data Analysis Techniques

To understand the data and see any correlations or similarities, this study uses analysis of variance (ANOVA) testing. The ANOVA assumptions include normally distributed and homogenous variance. The Box and Whiskers (in text and Appendix F) show skewed distributions, but due to a small size ANOVA was still used. ANOVA testing is a statistical analysis approach that can be used to measure the difference between two or more data sets. The equation used for the ANOVA method is listed below in Equation 1.

$$Y_i = \mu + \alpha_t + \beta_j + \alpha_t \beta_j + \varepsilon_{ij} \quad (1)$$

In Equation 1, Y_i is the variable under investigation. μ is the overall mean and is used to characterizing the mean value, but is not well or time dependent. α is the variable that represents each well and β is the time component. $\alpha_t \beta_j$ represents the intercept of the wells but can be eliminated if the p-value is less than 0.05, which is the designated value for determining statistical difference. The ANOVA method outputs a p-value that corresponds to either the hypothesis being acceptable (usually $p<0.05$). If the $p>0.05$, then the alternate hypothesis is correct. The alternate hypothesis is that the recycled wells are significantly different, and the null hypothesis is the wells are not significantly different. ANOVA uses linear regression to determine the similarities in the data sets and can be seen in equations 2 through 5.

$$H_o: \alpha_1 = \alpha_2 = \alpha_3 \quad (2)$$
$$H_A: \alpha_1 \neq \alpha_2 \neq \alpha_3 \quad (3)$$

$$H_o: \beta_1 = \beta_2 = \beta_3 \quad (4)$$
$$H_A: \beta_1 \neq \beta_2 \neq \beta_3 \quad (5)$$

Equations 2 and 3 indicate the null hypothesis that the wells do not show a statistical difference and the alternate hypothesis is that they are statistically different. The ANOVA tests whether there is a difference in well chemistry. Equations 4 and 5 shows the same statistical test but for the wells over time. For the time portion of the ANOVA results, the method takes an average of the data points in that time period. The time periods are broken down into three groups. The first time group is days 1-7 and is labeled as early time period. The second time period groups days 8-13 and labeled as middle time period. The third time period includes days 14-29.

A simple linear regression model was used to estimate similarities of produced water quality (Eqn.6) between each recycled well and the fresh water well. This linear regression was used as another method for inorganic data analysis.

$$Y = \beta_1 + \beta_2 X \quad (6)$$

In this model, dummy variable D_1 and D_2 were used, which were both set to 0 if the water quality parameters come from Well F, D_1 was 1 and D_2 was 0 if the data came from the water quality parameters from Well R1, and D_1 was 0 and D_2 was 1 if the data came from the water quality parameters from Well R2. That is,

$$\begin{cases} D_1 = 0 \text{ and } D_2 = 0, \text{if data come from Well F} \\ D_1 = 1 \text{ and } D_2 = 0, \text{if data come from Well R1} \\ D_1 = 0 \text{ and } D_2 = 1, \text{if data come from Well R2} \end{cases} \quad (7)$$

By combining Equations (6) and (7), the following equation is obtained:

$$Y = \beta_1 + \beta_2 X + (\beta_3 + \beta_4 X) \times D_1 + (\beta_5 + \beta_6 X) \times D_2 \quad (8)$$

Where $\beta_1, \beta_2, \beta_3, \beta_4, \beta_5$ and β_6 are fitting coefficients and D_1 and D_2 are dummy variables. Three different equations were acquired based on the ratio of fresh water and recycled water used:

$$Y_{\text{well F}} = \beta_1 + \beta_2 X \quad (9)$$

$$Y_{\text{well R1}} = (\beta_1 + \beta_3) + (\beta_2 + \beta_4) X \quad (10)$$

$$Y_{\text{well R2}} = (\beta_1 + \beta_5) + (\beta_2 + \beta_6) X \quad (11)$$

The null hypothesis for the linear regression model was that coefficient β_i is zero and the alternative hypothesis was that β_i is not zero. Coefficients β_1, β_2 are fitting constants for Well F, coefficients β_3, β_4 are fitting constant for Well R1 and coefficients β_5, β_6 are fitting constant for Well R2. Coefficients β_3 and β_4 indicate a statistically significant difference between Well F and Well R1 and coefficients β_5 and β_6 indicate a statically significant difference between Well F and Well R2. Relatively lower values for the coefficient of determination (R^2) indicate water quality parameters of temporal variability from three wells

were not strongly related. For wells having the same y-intercept means the fresh water well and the recycled wells have the statistically similar starting values at time equals zero, which might indicate that the ratio or recycled to fresh water does not affect the constituent in question. If the slopes are same, then that could indicate the wells are affected by the geological formation at the same rate.

3.5 Results

This section will detail the results of the analysis on the produced water samples taken from Well F, R1 and R2. The data will be presented in graphs, the ANOVA results and the other statistical method utilizing linear regression. The data will be presented as figures in this section or in Appendix B.

3.5.1 Gravimetric Solids and Turbidity

Table 3-3 displays the minimum, maximum and average for TS, TDS and TSS. Figure 3-1 shows box plots for TSS, TDS and TS. Figure 3-2 below provides the temporal data for TSS, TDS and TS. It begins at day one of sampling and continues through day 29.

Table 3-3. Total Solids for All Three Wells Sampled

	Total Solids (TS)			Total Dissolved Solids (TDS)			Total Suspended Solids (TSS)		
	Well F	Well R1	Well R2	Well F	Well R1	Well R2	Well F	Well R1	Well R2
Min	9,020	12,900	14,920	12,960	12,880	14,420	48	44	129
Max	17,260	18,820	40,060	23,080	17,960	22,840	1,229	532	500
Average	15,139	16,696	19,562	15,354	16,189	17,887	362	230	236

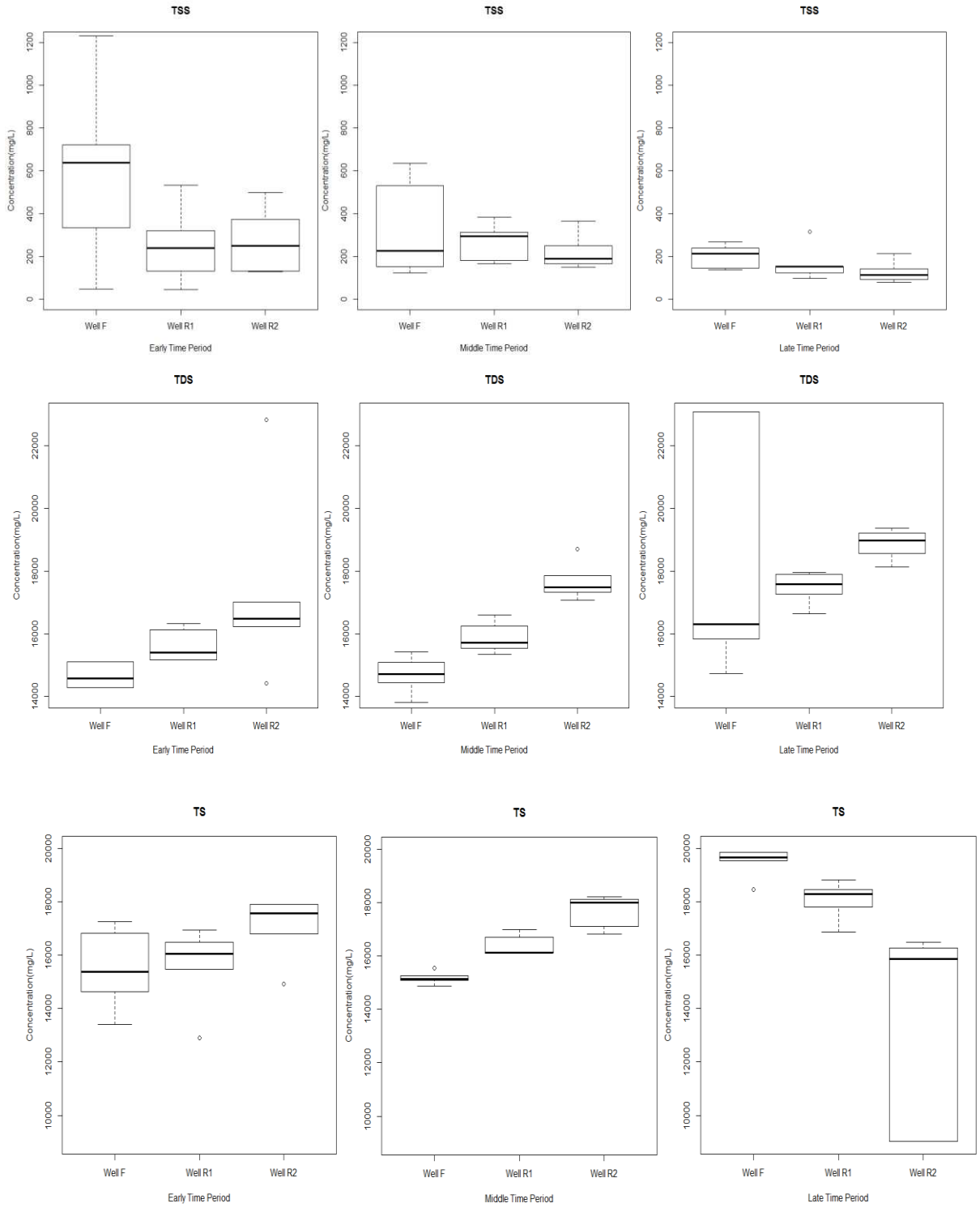


Figure 3-1. Box Plot of Data Points in TSS, TDS and TS

Figure 3-1 clearly indicates that the TS is mainly influenced by the TDS of the samples due to the large difference in concentrations in the samples. For TSS, the Early Time Period has the largest ranges and maximums for all the wells. This type of variation was seen in the data from Crow Creek as well. The ranges and maximums decreased over time and was the smallest and had the lowest maximum concentration in the Late Time Period. For TDS, Well F had the largest range between its first and third quartile in the Late Time Period. The TDS was very similar in range and median during the Early and Middle Time Periods, and the wells' median values were in the same order during all three time periods. The order of the wells' median values was the same for the Early and Middle Time Periods, but flipped for the Late Time Period.

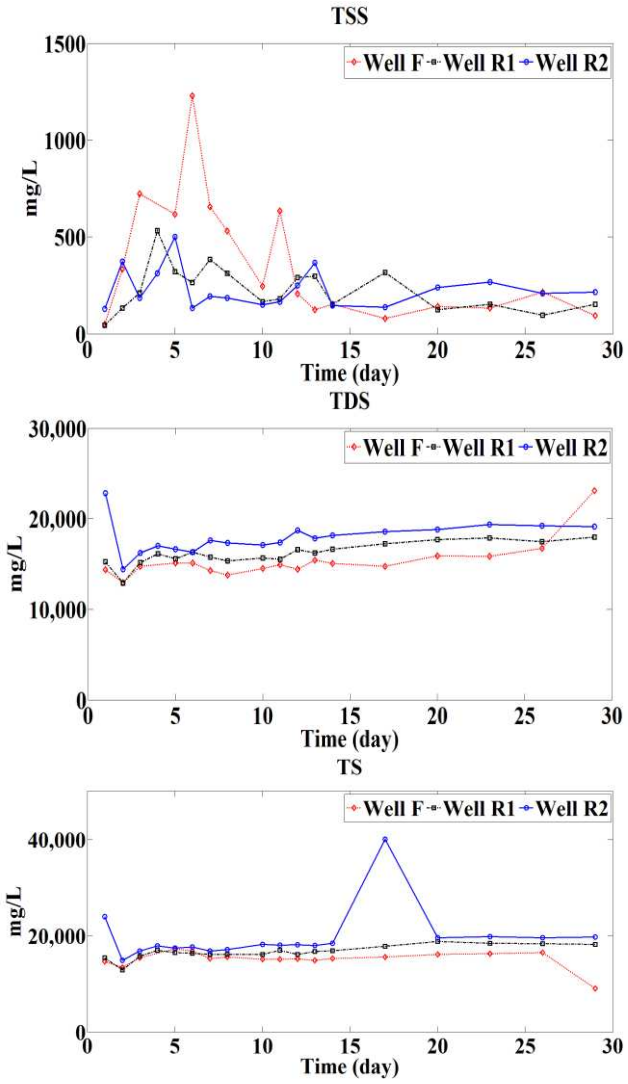


Figure 3-2. Comparison of the Three Wells for TSS, TDS and TS

TS shows a slight increase over time with the recycled wells higher than Well F. TDS shows a similar trend to TS in that all three wells appear to trend upward over time. For TDS, the recycled wells again had higher values than the fresh water well. Table 3-3 shows the recycled wells have higher average TDS and TS than Well F. For the TSS, Well F has a much higher value with a more sporadic nature in the beginning of the sampling, which causes Well F to have a higher average despite being in line with the other wells after day 10. TSS makes a

smaller portion of the TS, as can be noted by the significantly lower mg/L values meaning the higher TDS for the recycled wells affects the TS more and the recycled wells have higher TS.

Table 3-4 shows ANOVA testing data for TDS, TSS and TS. The TDS shows that there is a significant difference between the wells and over time. This indicates that the TDS was affected by the fracturing fluid and the interactions underground with the geological formation.

Table 3-4. ANOVA Results for Gravimetric Solids

	Well effect		Time effect		Well and Time effect	
	F	P	F	P	F	P
TDS	7.951	0.001	11.581	<0.001	0.957	0.44
TS	3.204	0.002	3.204	0.233	2.579	0.409
TSS	3.204	0.070	3.204	0.004	2.579	0.044
TVS	3.204	0.593	3.204	0.576	2.579	0.262
VSS	3.204	0.062	3.204	0.007	2.579	0.050
VDS	3.204	0.447	3.204	0.014	2.579	0.278
Turb	3.204	0.490	3.204	0.347	2.579	0.052

Table 3-4 shows that the TDS is significantly different both between wells and over time. TS is significantly different between wells and TSS are different over time. The volatiles only significantly differed over time for VSS and VDS. The volatile portion of the solids trends downward, the opposite of the previous three solids mentioned, as seen in Figure 3-2. Table 3-5 displays the data for all three volatile solids test for the three wells.

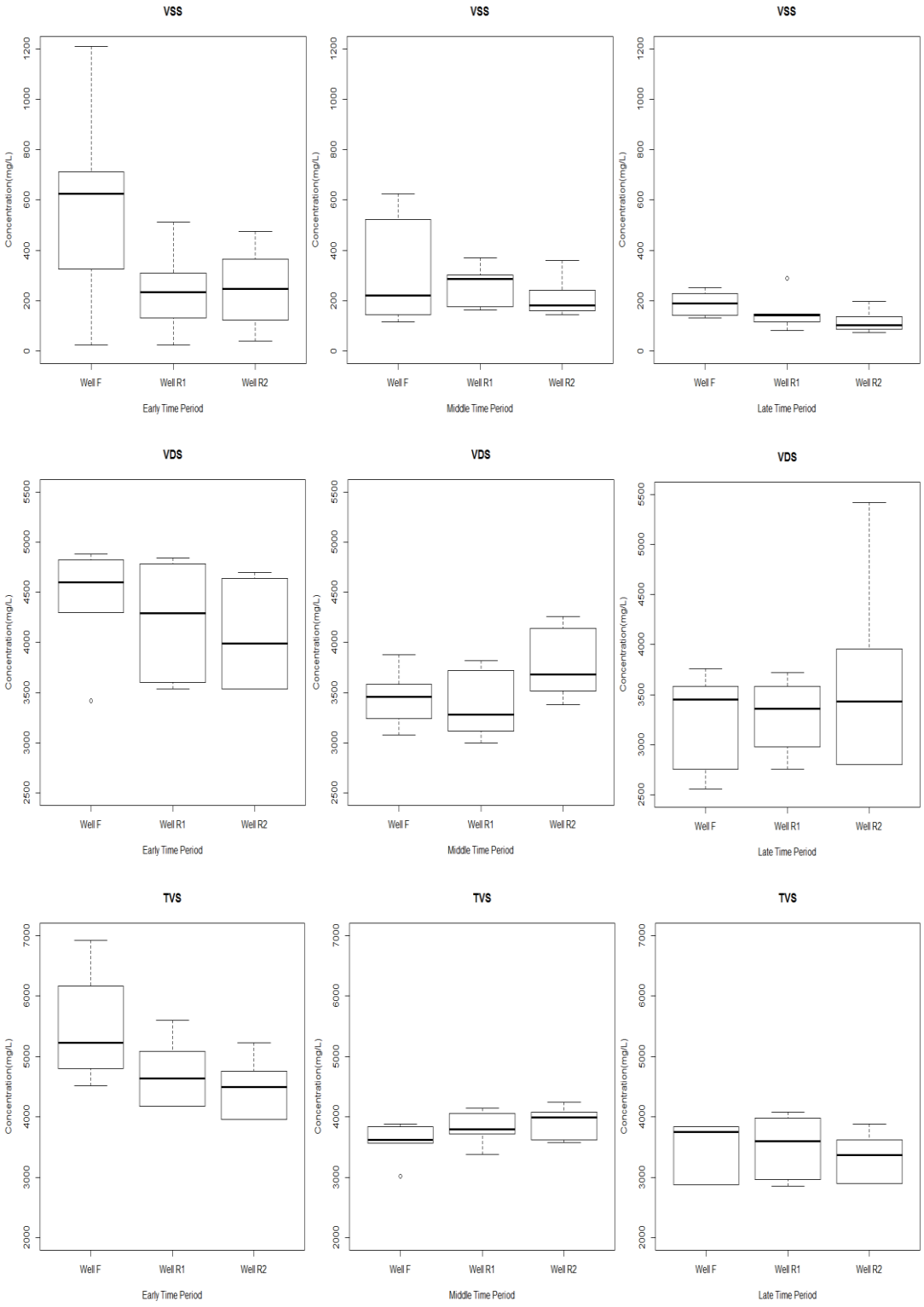


Figure 3-3. Box Plot of Data Points for VSS, VDS and TVS

For VSS in Figure 3-3, the time periods mirror the time periods seen in the TSS in Figure 3-1. The range and maximums are the highest in the early time periods and decrease as the time periods go to middle and late. Well R1 does show an increase in the median but the range between the maximum and the minimum decreases. VDS also sees a decrease in maximums, with the exception of Well R1.

Figure 3-4 shows that during the middle time period Well R2 had higher TVS measurements.

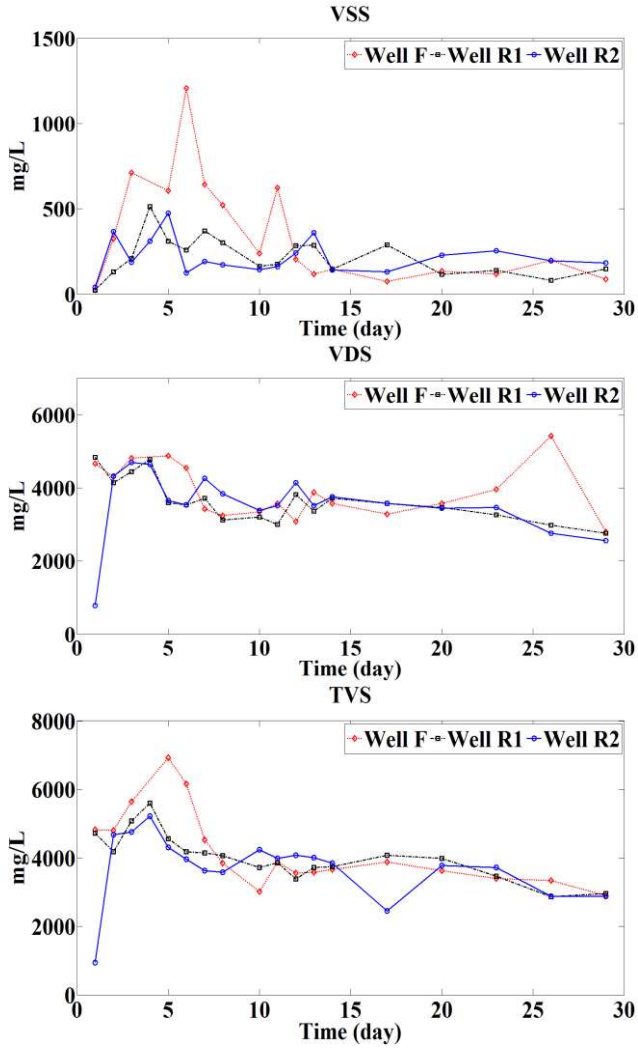


Figure 3-4. Temporal Trends of TVS, VDS and VSS

Table 3-5. Volatile Solids Data

	Total Volatile Solids (TVS)			Volatile Dissolved Solids			Volatile Suspended Solids		
	Well F	Well R1	Well R2	Well F	Well R1	Well R2	Well F	Well R1	Well R2
Min	2,900	2,860	940	2,800	2,760	780	25	23	41
Max	6,920	5,600	24,480	5,420	4,840	4,700	1,208	513	474
Average	4,208	4,016	3,792	3,904	3,629	3,546	352	219	222

As the data shows in Table 3-5, Well F has higher maximums and averages for all three volatile analyses performed. The TVS and VSS for Well F followed the same path as it did for TSS with a high amount of variability in the first 10 days. The TVS and VSS, just like the TSS, becomes more consistent as the well ages and likely indicates that the early flowback was influenced by the fracturing fluid makeup and the cause of the fluctuations. The TVS and VDS do not appear to be as affected by the fracturing fluid as the variability is less pronounced, and this is also the case for the TS and TDS.

The high value for TVS on Well R2 is on the same day's sample as the high value for TS. This likely indicates that either the numbers are correct or that the sampling from the well head produced an inconsistent sample that does not match the rest of the samples.

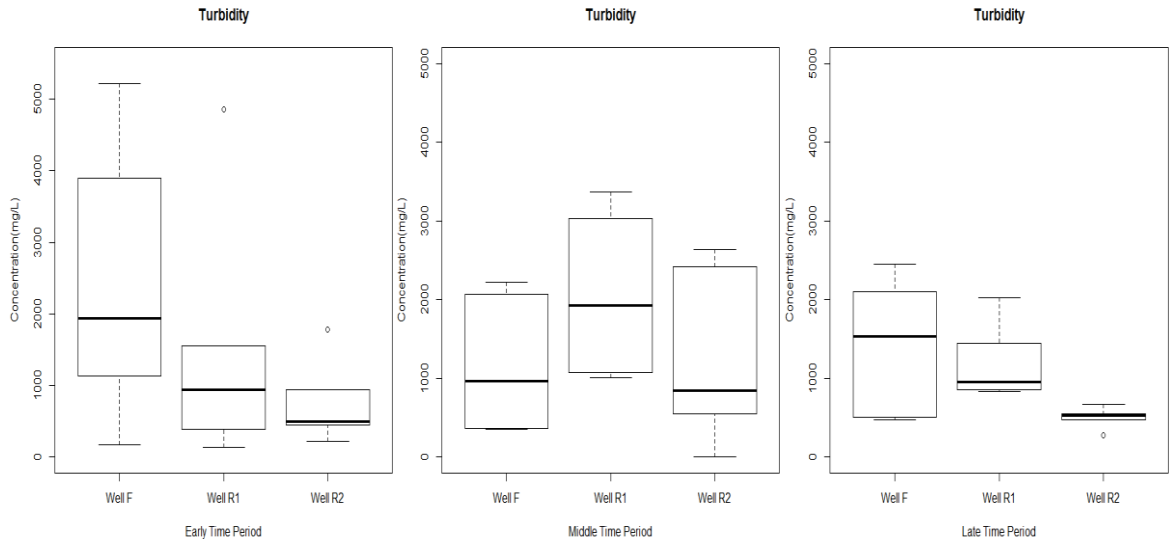


Figure 3-5. Box Plot of Data Points in Early, Middle and Late Time Periods for Turbidity

For turbidity, the box plots, shown in figure 3-5, show that Well F has a higher turbidity in the Early and Late Time Periods than the Middle Time Period. Well R1 has the higher turbidity over R2 in all three time periods when comparing just the two recycled wells. All three wells decrease their range when looking only at the Early to the Late Time Periods, but the Middle Time Period had a higher range and maximum in the Middle Time Period.

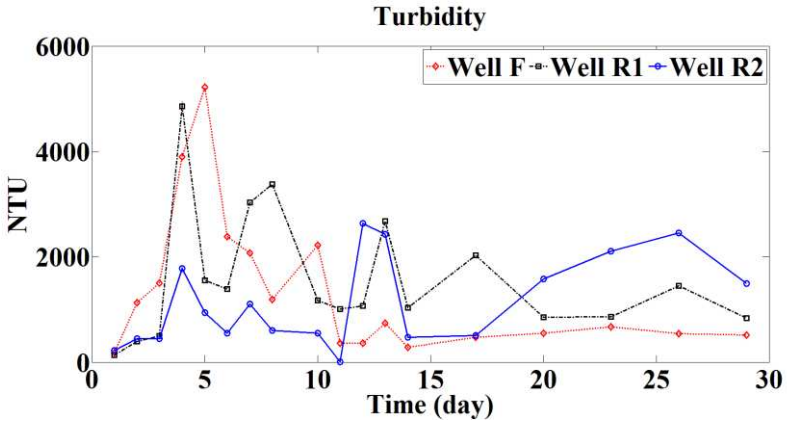


Figure 3-6. Turbidity's Temporal Trend

For turbidity, the data, seen above in Figure 3-6, is not consistent. All three wells show high variability with no real trend toward increasing or decreasing. However, Well F does

become the most stable from day 11 through the rest of the sampling. Well R2 has the smallest gap between its minimum and maximum, but fluctuates more than Well F. The temporal variability throughout the sampling indicates a strong interaction with the geologic formation. Table 3-4 shows that there is no significant difference between the wells or over time.

3.5.2 TOC and DOC

Figure 3-7 shows the box plot data for TOC and DOC data is in Figure 3-8. Figure 3-9 shows the temporal trends for TOC and DOC.

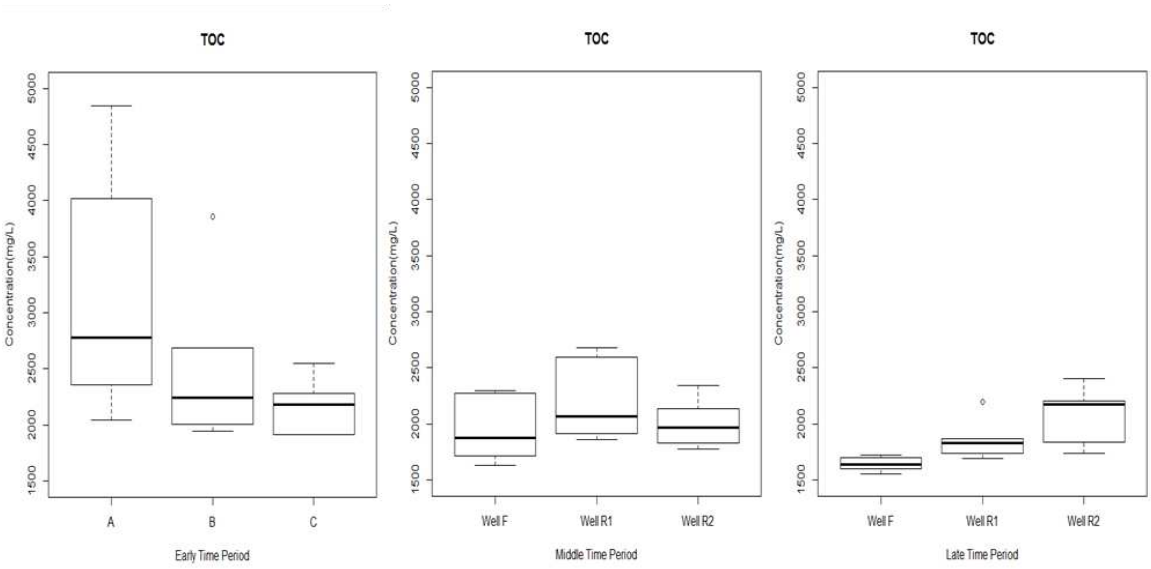


Figure 3-7. Box Plot of Data Points in Early, Middle and Late Time Periods for TOC

The early time period showed the TOC in Well F to be the highest with Well R1 and R2 just over 2000 mg/L. By the late time period, Well R2 was hundreds of mg/L higher than Well R1 which was also hundreds of mg/L higher than Well F. The decrease in range of the samples in the Late Time Period is consistent with the data gathered at Crow Creek. The smaller range indicates that the samples were more consistent and had a lower concentration than the other time periods except for Well R2.

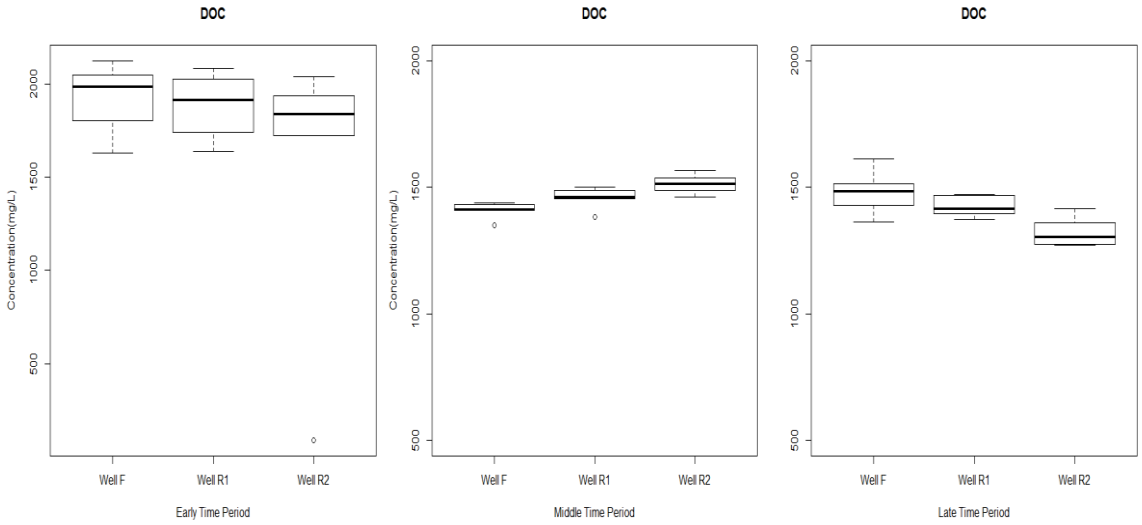


Figure 3-8. Box Plot of Data Points in Early, Middle and Late Time Periods for DOC

Figure 3-10 shows that Well F had the highest median for the Early Time Period, but the recycled wells were not that much less. The wells' ranges were the smallest in the Middle Time Period and then the Late Time Period had the next smallest ranges. The median values decreased from the Early to the Middle Time Periods but stayed roughly the same from the Middle to the Late Time Periods.

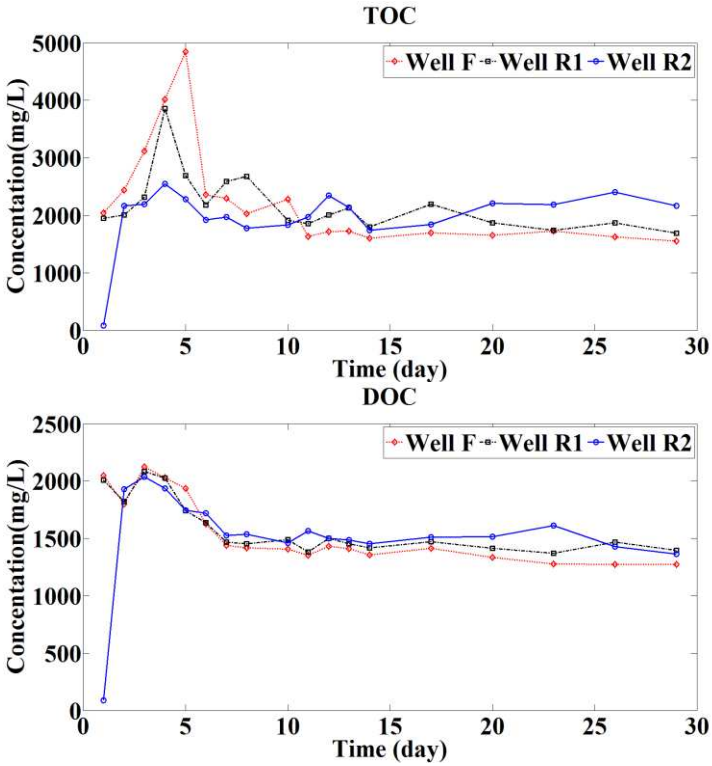


Figure 3-9. TOC and DOC Temporal Trends

For TOC, Well F again showed early variability, meaning that it is likely heavily influenced by the fracturing fluid, before becoming steady after day 10 and was the lowest of those three wells after day 10. However, Well F had the highest TOC value for the first six samples. Well R1 also peaked in the early portion of the sampling before finishing with a slightly higher TOC value than Well F on the last sample point. Both Wells F and R1 appear to decline over time. Well R2 again was the most stable throughout the sample but had the highest TOC value of all three wells over the last 10 days of sampling. TOC was analyzed using the ANOVA method and showed no significant difference between the three wells but did significantly differ temporally. Table 3-6 shows the ANOVA results for TOC and the oil based organics.

Table 3-6. ANOVA Data

	Well effect		Time effect		Well and Time effect	
	F	P	F	P	F	P
TOC	1.024	0.367	6.065	0.005	3.934	0.008
DOC	3.204	0.758	3.204	0.001	2.579	0.138
GRO	1.079	0.349	4.868	0.012	1.723	0.162
DRO	0.265	0.768	2.393	0.103	1.338	0.27
ORO	0.349	0.707	3.837	0.029	1.264	0.298
TPH	0.999	0.376	5.485	0.007	1.996	0.111

The DOC of the three wells, with the exception of day one for Well R2, showed similar data between them. All three wells had similar data from day two onward and all three showed a decline in DOC over time. The similarities in the slope means the interaction with the formation did not affect the DOC values.

As seen in Table 3-6, GRO, DRO, ORO and TPH did not vary significantly between the wells. However, all of these constituents, with the exception of DRO, were significantly different temporally. The difference was more pronounced earlier in the sampling period with more consistency in the samples beginning around day 15. The box and whisker plots for GRO, DRO, ORO and TPH can be found in Appendix F.

3.5.3 pH, Alkalinity and Carbohydrates

Figure 3-5 shows the trends for pH and alkalinity and Carbohydrates and Table 3.5 gives the pH minimum, maximum and average. The same data for alkalinity and carbohydrates is presented in Table 3-7.

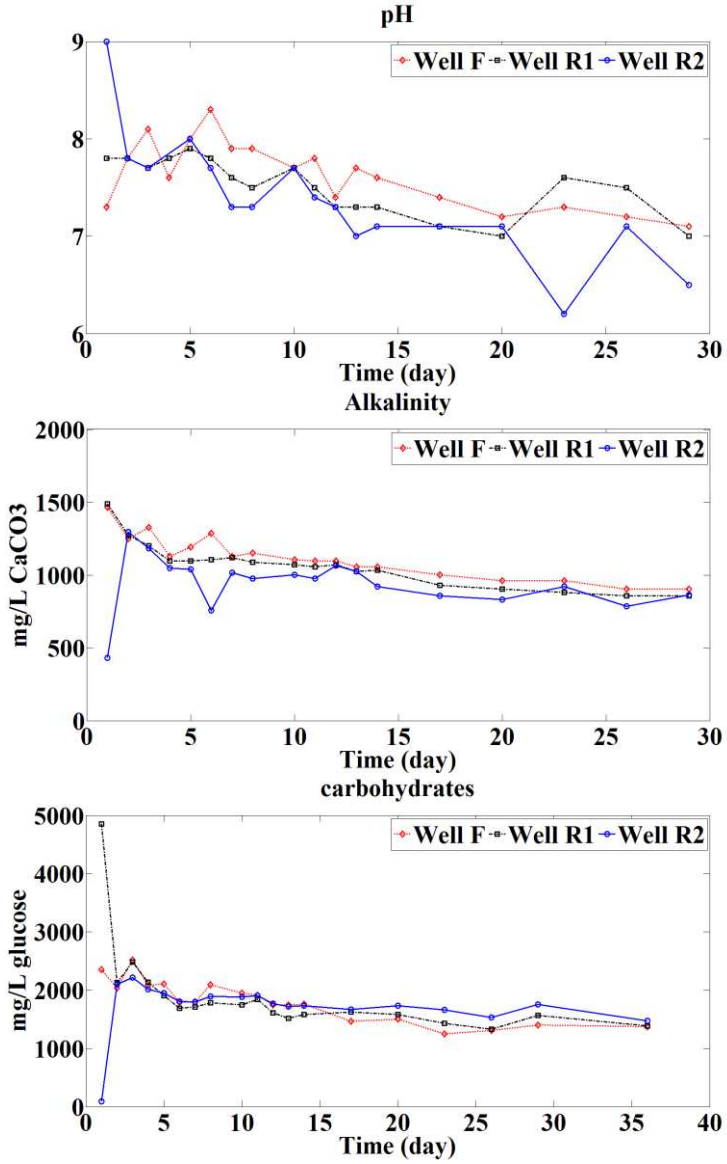


Figure 3-10. pH, Alkalinity and Carbohydrates Temporal Trends

Table 3-6. pH, Alkalinity and Carbohydrates Data

	pH			Alkalinity			Carbohydrates		
	Well F	Well R1	Well R2	Well F	Well R1	Well R2	Well F	Well R1	Well R2
Min	6.78	6.69	6.64	904	856	432	1248	1330	88
Max	7.59	7.28	8.49	1464	1488	1296	2518	4852	2214
Average	7.07	6.946	7.03	1115	1064	944	1799	1891	1720

The pH for all three wells declined over time toward neutral. The data were sporadic throughout the sampling showing the geological interactions have a large impact on the pH. In

Table 3-6, the range for minimum, maximum and the average shows that all three wells are similar. This is confirmed by the ANOVA, seen in Table 3-7, test that did not show a statistical difference between the three wells, but it did indicate a significant difference temporally despite all three having a downward trend.

Table 3-7. ANOVA Data

	Well effect		Time effect		Well and Time effect	
	F	P	F	P	F	P
pH	3.186	0.051	24.512	<0.001	1.557	0.202
Alkalinity	8.279	<0.001	15.331	<0.001	1.716	0.163
Carbs	3.204	0.531	3.204	0.004	2.579	0.088

The alkalinity for Well F is higher than the other two wells for most of the sampling period. This fact is indicated by the highest average of the three wells. All three wells trend down over time. Well R2 is the lowest for most of the sampling. In the ANOVA analysis, the wells show a statistically significant difference between the three wells and over time.

For Carbohydrates, there is not a discernable difference in the graphs as the data points overlap and stay in a tight group at every data point except for the first day when Well R1 was very high and R2 was very low. The tight group shows that the fracturing fluid does not affect the interaction with the formation over time, verified by the ANOVA testing in Table 3-7. All three wells showed a decline in carbohydrates over the sampling period. The carbohydrate decline over time indicates that the wells wastewater is transitioning from flowback, heavily influenced by the fracturing fluid, to produced water, heavily influenced by fracturing fluid's interaction with the geological formation. This could explain why Well F's water quality stabilized after day 10 of the sampling more so than the recycled wells. The fresh water might have a higher ability to solubilize material and therefore the initial timeframe would be varied

as the water interacts with the additives and the reservoir. However, the ability to solubilize does not affect organic matter that would show up in DOC.

Figures 3-11 through 3-13 shows the box and whisker plots for pH, alkalinity and carbohydrates.

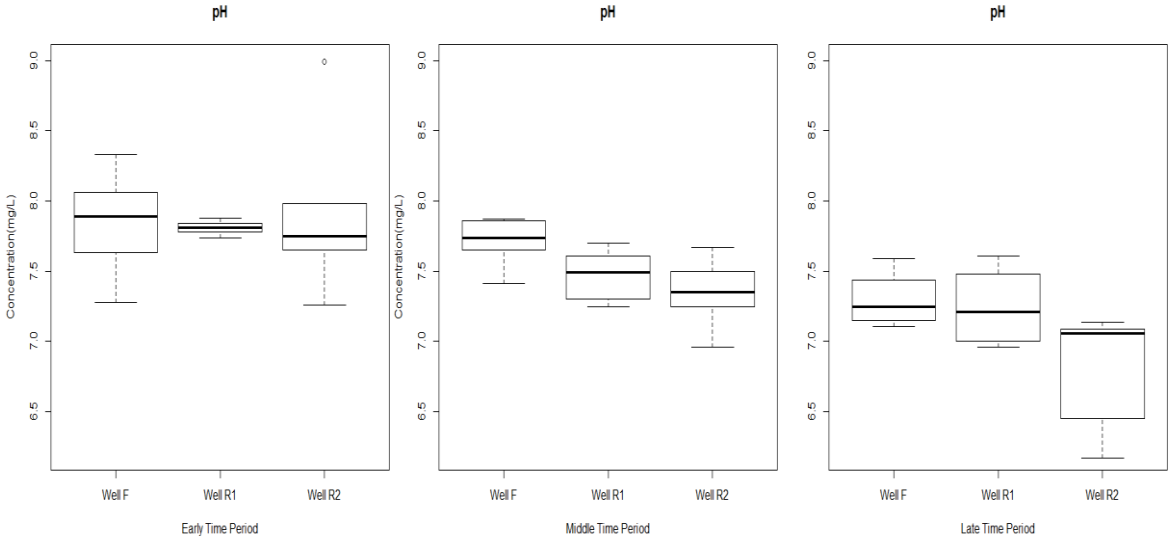


Figure 3-11. Box Plot of Data Points in Early, Middle and Late Time Periods for pH

The pH data shows that Well F has a higher median in all three time periods. Well R1 is again the middle value for all three time periods. All three wells declined their medians and maximums toward neutral from the Early to the Middle and Late Time Periods.

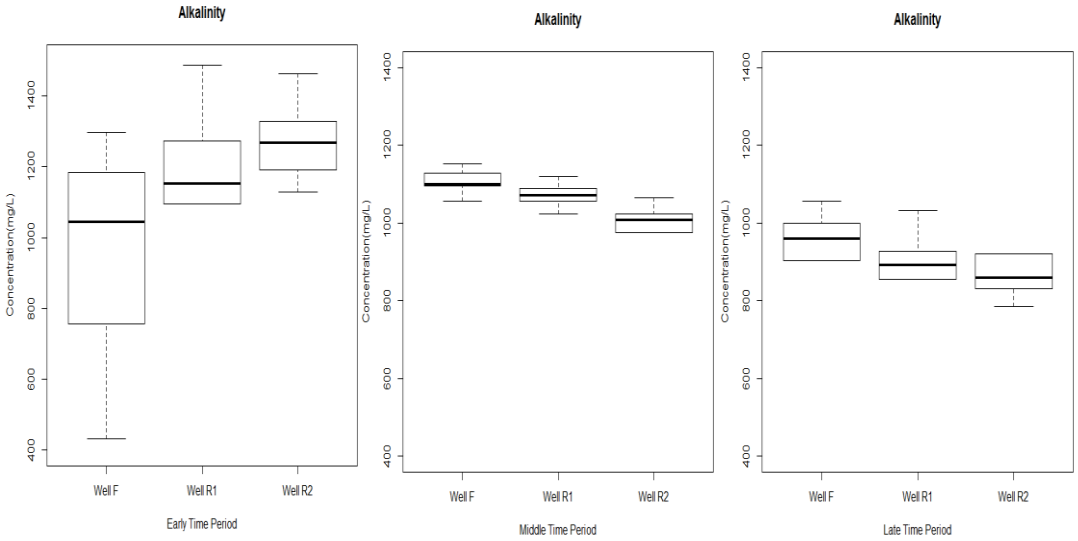


Figure 3-12. Box Plot of Data Points in Early, Middle and Late Time Periods for Alkalinity

Again, the box plots in Figure 3-12 show that Well R1 is the middle value over all three time periods. Well R2 was the highest in the early time period. Well F had a higher alkalinity than the other two wells in the Middle and Late Time Periods. The Late Time Period had the lowest Maximums, but the Middle Time Period was the most consistent sampling as seen by the small ranges between first and third quartiles.

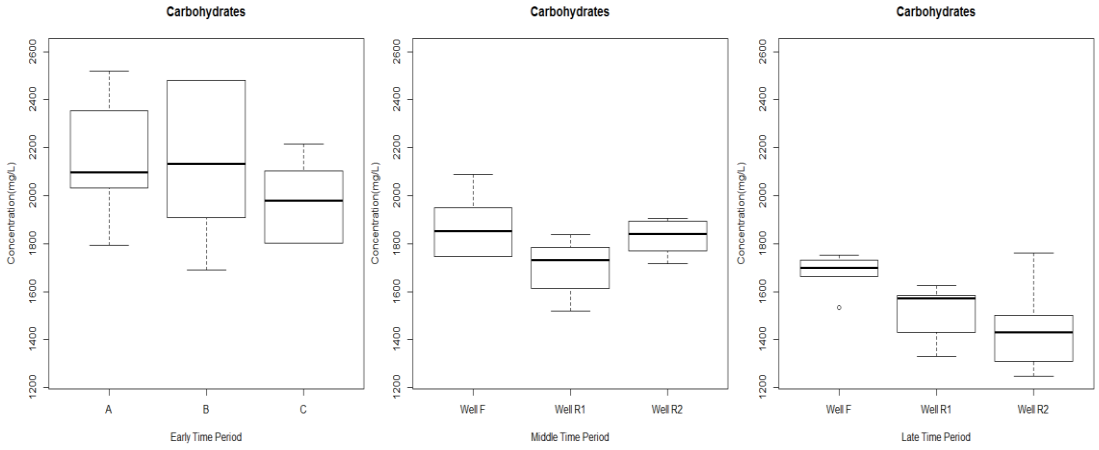


Figure 3-13. Box Plot of Data Points in Early, Middle and Late Time Periods for Carbohydrates

The carbohydrate box and whisker plots in Figure 3-13 show a decline from Early through Middle and into the Late Time Periods, just like in the pH plots. All three wells were at one point the highest, the middle and lowest well in terms of median values, which shows that the wells' base fluid likely did not play a part in the carbohydrate portion of the produced water.

3.5.4. LC-MS

LC-MS and the Agilent mass hunter qualitative analysis were performed to analyze flowback water samples of 1 day, 2days, 6 days, 10 days, 14 days and 20 days from Well F, Well R1 and Well R2. Figure 3-14 presents the LC-MS-ESI-Positive ion spectrum. The spectrum shows that they have almost the same peaks for all three wells with temporal variability but different relative abundances except for day one's sample from the well R2. This might be because the day one sample for Well R2 was collected from the well head. Figure 3-15 shows the mass spectra of flowback samples from Well F for days 1, 2, 6, 10, 14 and 20, and the rest of the wells' mass spectra can be found in Appendix C. Similar organic compounds were detected at each well and no temporal trends in the data are evident.

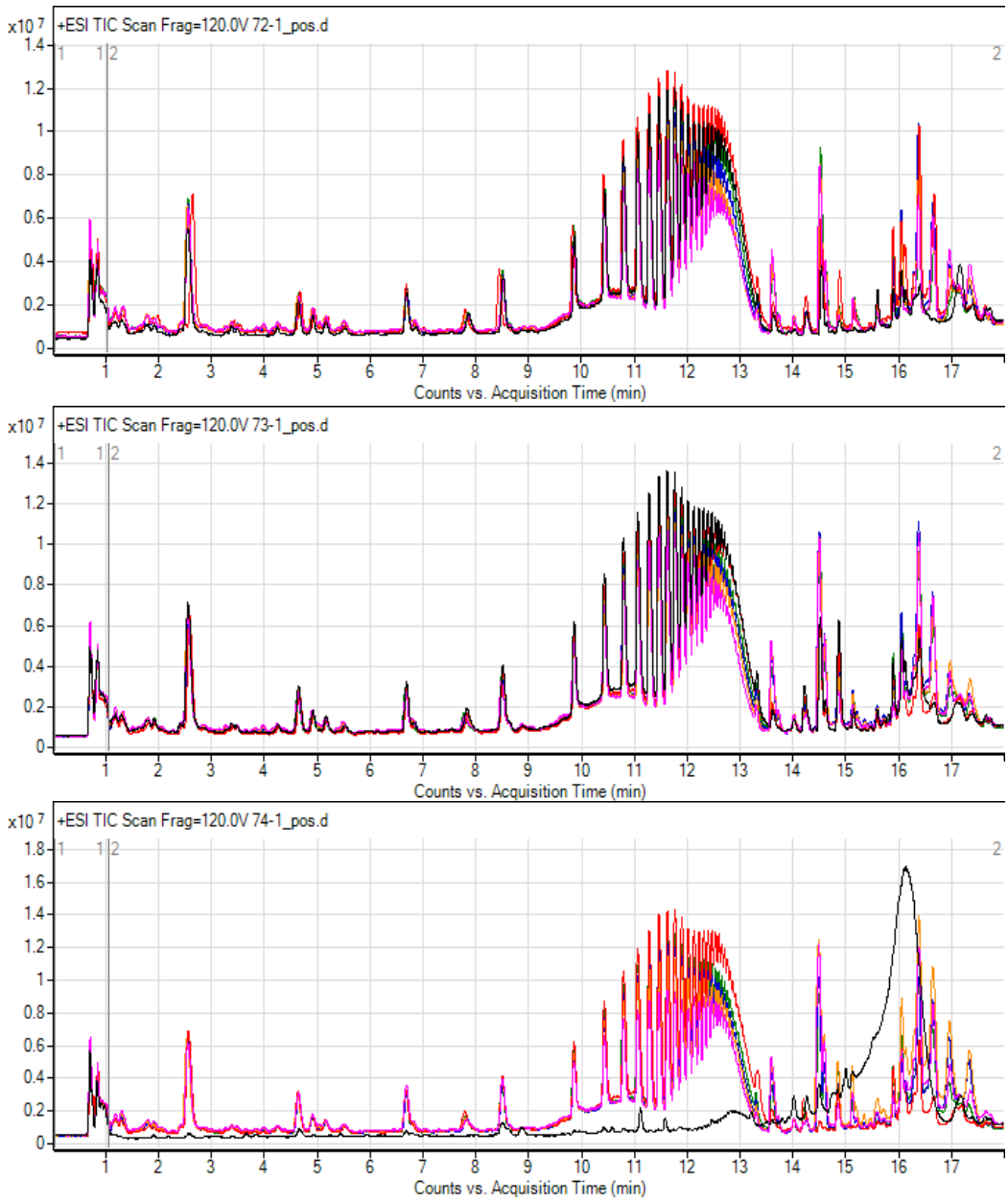


Figure 3-14. LC-MS-ESI-Positive Ion Spectrum for All Wells

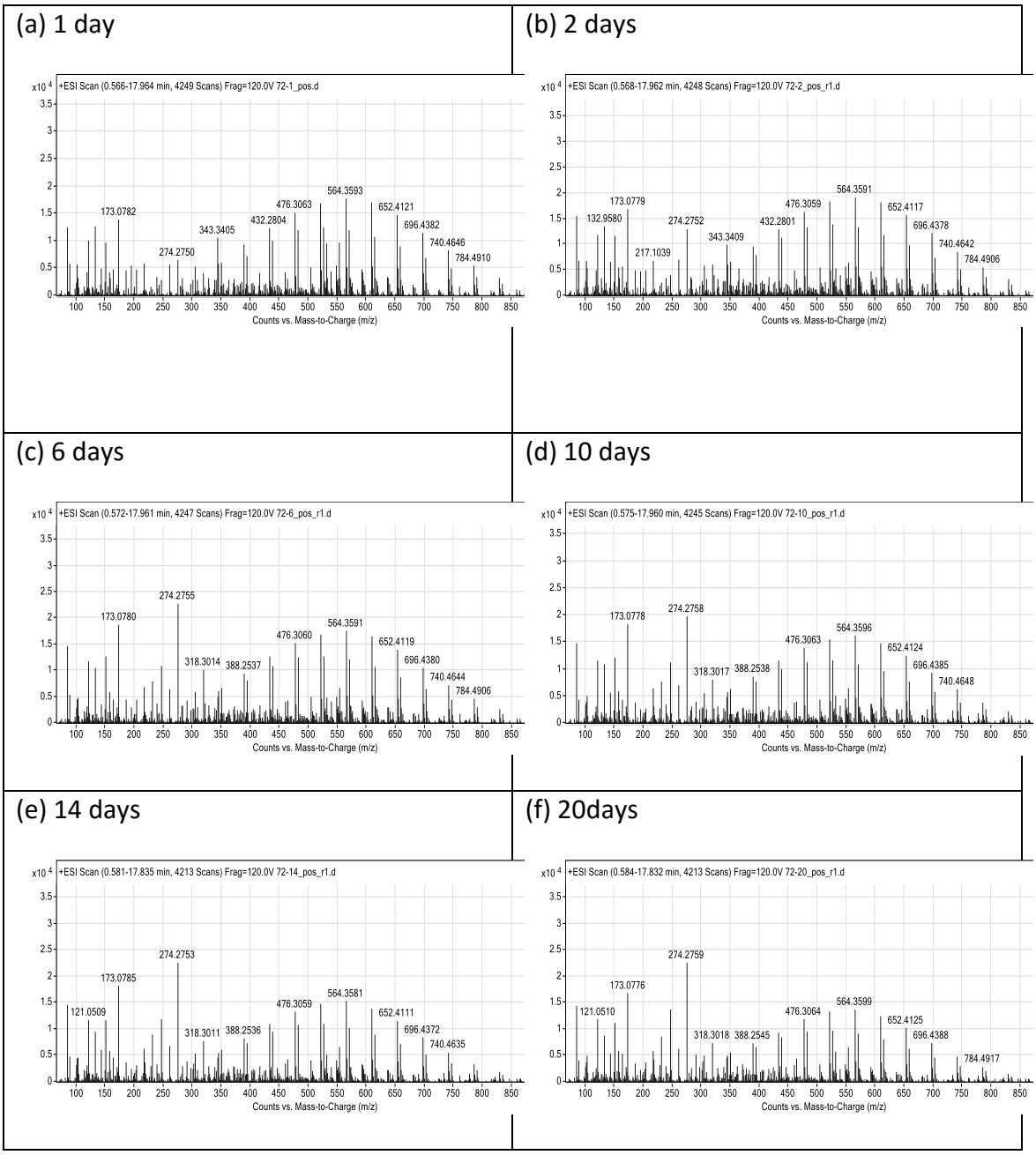


Figure 3-15. Mass Spectrum of Flowback from Well F

The LC-MS-ESI-Negative ion spectrum is located in Appendix C and shows a similar pattern to the positive ion spectrum for each of the wells have peaks at similar retention times and little difference of abundance, and even shows the same problem with Well R2's day one sample. The mass spectra of LS-MS-ESI-negative ion may also be found in Appendix C. This data

again shows similarities for organic compounds that were detected at each well similar to the results of LC-MS-ESI-Positive ion.

More organic compounds were detected in LC-MS-ESI-Positive mode than LC-MS-ESI-Negative mode. The detected organic compounds from the negative mode are shown in Table 3-8. When the column has an F in it, then the compound was present in Well F. The same procedure is used for R1 and R2, which indicates Well R1 and Well R2, respectively. Any box that contains the word "ALL" indicates the compound was found in all three wells on that day of sampling. The LC-MS-ESI Positive data is presented after the negative in Table 3-9.

Table 3-7. Compounds Found in the Samples Via LC-MS-EIS Negative Characterization

	1 day	2 days	6 days	10 days	14 days	20 days
Acrylic acid, 2-hydroxyethyl ester	F, R1	ALL	F, R2	ALL	ALL	F, R2
Adipic acid		F, R1	ALL	ALL	ALL	R1, R2
Benzenecarboperoxoic acid, 1,1-dimethylethyl ester	F, R2	ALL	F, R1	ALL	F	R1
Benzoic acid		F, R1	F	ALL	F, R1	ALL
Butyl lactate	ALL	ALL	ALL	ALL	ALL	ALL
Di (ethylene glycol) ethyl ether acetate		R2	R2	R2		
Diisopropylnaphthalenesulfonic acid	R2					
Dimethyl glutarate		F		F, R1	ALL	F, R1
Dodecylbenzene sulfonic acid	ALL	ALL	ALL	ALL	ALL	ALL
Ethyl acetoacetate	F	F	F	ALL	ALL	R1, R2
Fumaric acid		R2				
L-Dilactide		R2		R1, R2	R1, R2	R1, R2
Methyl salicylate	F, R1	ALL	R1, R2	F, R1	R1, R2	F, R1
Nitrilotriacetonitrile	F	ALL	ALL	ALL	ALL	ALL
Sodium diacetate	F	ALL	ALL	R2	ALL	R1, R2
Triamcinolone		F				

Most of the compounds appear to be present in all three wells. Some of the compounds do not appear on all the same days for all three samples, but since the compounds are present

for many of the same day's samples then those were considered to be present in all three wells. The compounds that were not present in all of the samples for more than one day were: Benzoic Acid, Di (ethyleneglycol) ethyl ether acetate, Dimethyle glutarate, ethyl acetoacetate, L-dilactide. Benzoic acid is present in all but the first day of Well F. Well R1 also did not show up in day six as well as day one like Well F. Well R2 showed benzoic acid in only two samples. Di (ethyleneglycol) ethyl ether acetate only showed up in Well R2 and on sample days two, six and 10. Dimethyle glutarate showed up in sample days 10, 14 and 20 for Wells F and R1, but only showed up on day 14 for Well R2. Ethyl acetoacetate was present in the first three samples for Well F but not the recycled wells. L-dilactide showed up on the last three samples for Wells R1 and R2, but not once in Well F.

Table 3-8. Compounds Found in the Samples Via LC-MS-EIS Positive Characterization

Organic Compounds	1 day	2 days	6 days	10 days	14 days	20 days
Ethoxylated oleyl amine	R1, R2	ALL	ALL	ALL	ALL	ALL
Ethyl acetoacetate	R1, R2		ALL	ALL	ALL	ALL
Ethylene glycol monobutyl ether (2-butoxyethanol)			F	ALL	ALL	ALL
Fumaric acid	R1, R2	F	R1, R2	R1, R2	R1, R2	R1, R2
Furfuryl alcohol			ALL	ALL	ALL	ALL
Glutaraldehyde	ALL	ALL	ALL	ALL	ALL	ALL
Methylcyclohexane	F	F		F	F	ALL
Phthalic anhydride	ALL	ALL	ALL	ALL	ALL	ALL
Polyethylene glycol	ALL	ALL	ALL	ALL	ALL	ALL
Polyethylene-polypropylene glycol						ALL
Progesterone						
Salbuterol	ALL	ALL	ALL	ALL	ALL	ALL
Sodium diacetate		R1, R2	R1, R2		F	
Sorbitan monooleate						ALL
Toluene	R1, R2	F				
Triethanolamine (2,2,2-nitrilotriethanol)	R1, R2	F			R1, R2	
Triethylene glycol	ALL	ALL	ALL	ALL	ALL	ALL
Triisopropanolamine	ALL	ALL	ALL	ALL	ALL	ALL

The LC-MS-ESI Positive Ion data showed similarities for all the organic compounds. The compounds that varied significantly are fumaric acid and methylcyclohexane. Fumaric acid appears to have a higher probability to appear in recycled wells and methycyclohexane appears to appear mainly in fresh water wells. Other data points where the organic compounds did not show up in all the samples on the same day only varied by one day or two. This data again illustrates that the fracturing fluid of wells does not affect the organic matter the wastewater produced.

3.5.5. eAnalytics Testing Analysis

The measured data provided to CSU by eAnalytics is analyzed using the two statistical methods described above. The results will be presented with the ANOVA method detailed first, followed by the other linear regression method to verify the ANOVA method.

3.5.5.1 Metals and Ammonia Data Analysis

The results of the ANOVA testing for the inorganic material found in the produced water can be found in Table 3-10. Figures 3-15 and 3-16 shows the box and whisker plots for ammonium and magnesium. These two plots were chosen to show one constituent that was found to be significantly between the wells and over time, magnesium, and the other with just being significantly different over time, ammonium. Table 3-11 provides linear regression method two data.

Table 3-9. ANOVA Results for Inorganic metals and Compounds

	Well effect		Time effect		Well and Time	
	F	P	F	P	F	P
Aluminum	0.962	0.39	2.262	0.116	0.104	0.98
Boron	6.767	**0.003**	12.385	**<0.001**	0.609	0.658
Barium	40.147	**<0.001**	55.979	**<0.001**	1.097	0.37
Bromide	5.91	**0.005**	16.475	**<0.001**	1.032	0.401
Calcium	42.26	**<0.001**	35.583	**<0.001**	0.459	0.765
Iron	11.682	**<0.001**	6.246	**0.004**	1.714	0.164
Potassium	22.295	**<0.001**	1.19	0.314	0.525	0.718
Magnesium	46.262	**<0.001**	56.151	**<0.001**	0.853	0.499
Chlorine	4.699	**0.014**	8.775	**<0.001**	0.597	0.666
Silicon	3.057	0.057	9.902	**<0.001**	0.489	0.744
Strontium	60.909	**<0.001**	81.32	**<0.001**	1.008	0.413
Zinc	2.696	0.078	0.3	0.743	0.399	0.808
Sodium	8.551	**<0.001**	20.364	**<0.001**	0.826	0.515
Ammonium	2.539	0.09	11.025	**<0.001**	2.331	0.07
Bicarbonate	16.563	**<0.001**	33.044	**<0.001**	0.112	0.978
Sulfate	0.005	0.995	1.457	0.244	0.386	0.817

Based on the ANOVA analysis, most of the inorganic material measured showed a statistically significant, in many cases a strongly significant, difference between the three wells. The only inorganic matter not found to be statistically different between the three wells was aluminum, silicon, zinc, ammonium and Sulfate. Silicon was the closest to being significantly different of those five with only 0.007 separating it from a significantly different classification. Aluminum and sulfate were the only two that were not within 0.04 from being different between the three wells. Temporally, the results were similar with only four inorganic values found to not be significantly different. Those four include aluminum, potassium, zinc and sulfate. All four of these showed a p-value of much higher than 0.05 and therefore can be considered similar between the three wells.

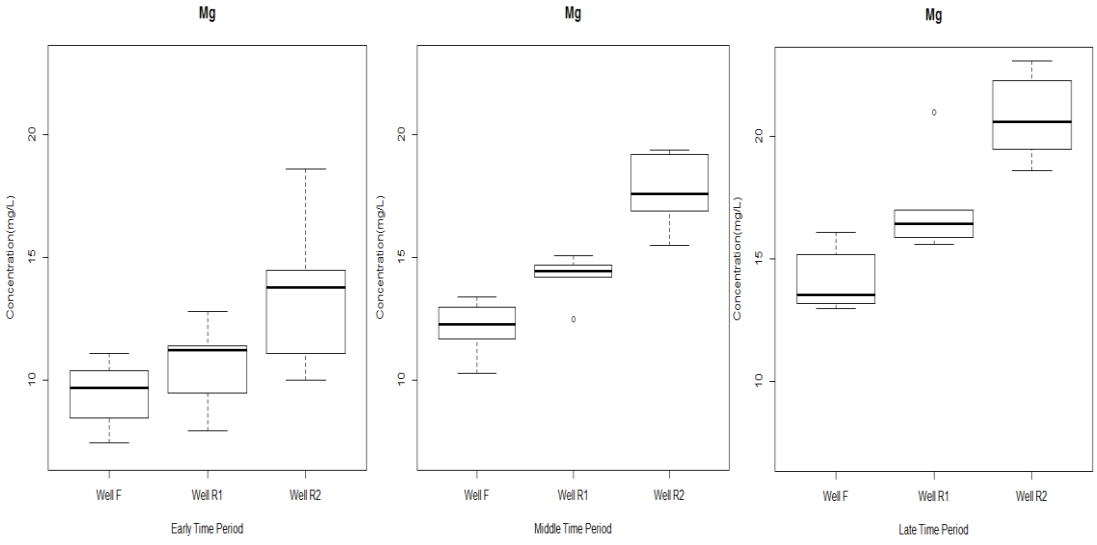


Figure 3-15. Early, Middle and Late time period Magnesium

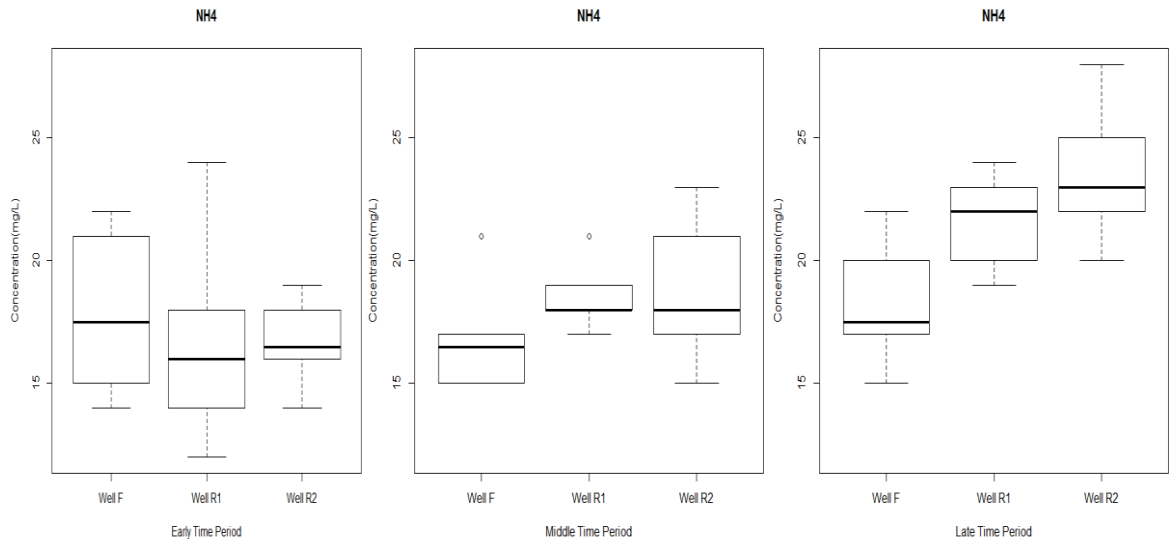


Figure 3-16. Box Plot of Data Points in Early, Middle and Late Time Periods for Ammonium

Figure 3-16 Well F had the largest range between the first and third quartile in the Early Time Period, but Well R1 had the highest maximum during the Early Time Frame and Well R2 had the highest maximum in the Late Time Period. The Middle and Late Time Period showed that Well F was the lowest, its maximum was less than or equal to the medians of the other two wells in the Late Time Period. The fluctuation of the wells is likely why the ANOVA results show no significant difference between the wells. Figure 3-17 showed consistency in that Well F had the lowest median through the three periods, Well R1 was in the middle range for all three and Well R2 was the highest. The consistent difference in the box and whisker plots between the wells and over time is a good example to verify the ANOVA results.

Table 3-10. Linear Regression Statistical Method

	β_1	p-value	β_2	p-value	β_3	p-value	β_4	p-value	β_5	p-value	β_6	p-value	R
Aluminum	0.58	<0.01	0.002	0.75	-0.09	0.59	0.001	0.93	0.04	0.81	0.002	0.88	0.81
Barium	3.80	<0.01	0.08	<0.01	0.98	0.06	0.05	0.09	0.91	0.08	0.060	0.06	0.72
Boron	13.88	<0.01	0.04	0.51	-0.65	0.68	0.09	0.36	1.07	0.49	0.06	0.55	0.18
Br	25.63	<0.01	0.39	<0.01	4.59	0.06	-0.09	0.53	4.61	0.06	0.04	0.80	0.52
Bicarbonate	1192.84	<0.01	-10.0	<0.01	-77.37	0.20	2.97	0.42	-232.4	<0.01	5.06	0.17	0.51
Calcium	67.15	<0.01	1.20	<0.01	5.87	0.42	0.40	0.37	36.36	<0.01	0.09	0.84	0.74
Chloride	5062.01	<0.01	83.80	<0.01	1114.00	0.02	-25.22	0.36	927.9	0.04	21.47	0.44	0.61
Iron	32.52	<0.01	-0.25	0.18	-1.74	0.69	0.48	0.07	-14.20	<0.01	0.67	0.02	0.33
Magnes	9.06	<0.	0.2	<0.	0.70	0.5	0.0	0.1	5.02	<0.	0.0	0.4	0.

ium		01	0	01		1	9	5		01	5	1	78
Potassium	56.25	0.74	-0.36	0.97	12.53	0.96	0.46	0.97	521.54	0.04	-23.99	0.11	0.14
Sodium	3231.02	<0.01	49.79	0.01	907.44	0.03	-29.76	0.23	433.31	0.29	8.54	0.73	0.35
Strontium	9.37	<0.01	0.26	<0.01	0.81	0.41	0.08	0.17	3.87	<0.01	0.15	0.02	0.86
Sulfate	30.60	0.04	-0.45	0.61	3.01	0.88	-0.09	0.94	44.59	0.03	-2.27	0.07	0.19
Silicon	47.74	<0.01	-0.25	0.23	-1.37	0.77	0.10	0.72	-0.82	0.86	0.17	0.56	0.05
Zn	0.77	0.03	-0.01	0.65	1.13	0.02	-0.04	0.15	0.06	0.90	0.02	0.50	0.17
NH4	15.57	0.01	0.12	0.74	-0.76	0.93	0.16	0.76	16.31	0.06	-0.61	0.25	0.1

If p-value in bold is higher than 0.05, the constant β_i is not significant constant.

The linear regression showed some disparity for the inorganic compounds measured than those for the ANOVA of inorganic matter. Boron, barium, bromine, and silicon have p-values for Wells R1 and R2 that are higher than 0.05 and therefore are not significantly different. Bicarbonate, calcium, iron, magnesium, potassium, strontium, sulfate and silicon

showed no significant difference for Well R1. Sodium showed no significant difference for Well R2.

The Piper diagram is presented in Figure 3-18. The data points for all three wells overlap and are indistinguishable. The Piper diagram indicates that all three wells' produced water can be classified as brine with sodium, potassium and chlorine as the dominant species.

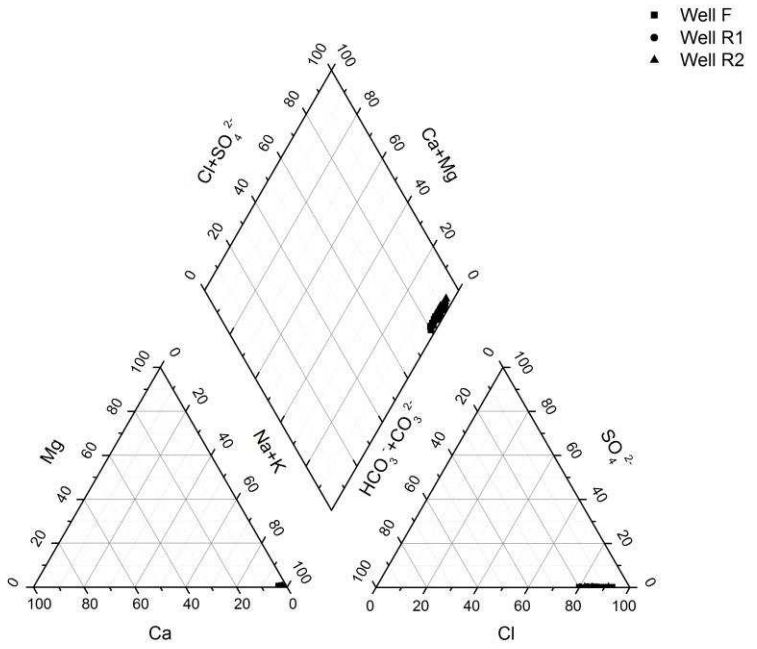


Figure 3-17. Piper Diagram of the Produced Water Data from the Three Wells

3.5.5.2. Organics, TDS and Alkalinity Data Analysis

The results of the ANOVA testing for organic material was much different than the inorganic analysis as almost all the data showed no significant difference between the three wells. Alkalinity and TDS were the only two tests that showed significant difference between the three wells. However, all of the wells showed a significant difference temporally for all the tests except for DRO.

4. CONCLUSIONS

The TS and TDS for Well F are lower than the recycled wells. This is likely due to the fracturing fluids used and the higher TDS of the recycled fluids. TDS had a much higher mg/L value than the TSS and therefore can be attributed to be main contributor to the TS.

The volatile portion of the solids measurement showed Well F to have the highest average for all three measurements TVS, VDS and VSS and shows that the fresh water has more organic solids than the recycled wells. This could be due to interaction with hydrocarbons in the reservoir.

The decrease in carbohydrates indicates a shift for the wells in what is the main contributor to TOC from flowback to produced water as the well matures. As the carbohydrates decrease, the TOC is shifting from the fracturing fluids being the largest contributors to the interaction with the hydrocarbons in the reservoir.

The base fluid in a fracture does not have an effect on pH and alkalinity. These factors could affect treatment strategies. The organic matter was not affected by the base fluid, fresh or recycled, of the fracturing fluid. This result was very different from the previous study done at the Crow Creek pad. There were multiple differences between the two studies including the use of different frac packages, PermStim (Crow Creek) and SilverStim (Chandler State). Additional research is being conducted to understand the differences.

5. FUTURE WORK

Due to the brevity of the sampling campaign and the use of PermStim versus SilverStim, definitive conclusions about the data are hard to make. Therefore, the first thing to consider is extending the sampling beyond the first month. The sampling does not have to continue indefinitely, but three to six months of data might allow for produced water characterization and not just flowback and early produced water. More wells would also be beneficial to verify data found at each well site.

A second option for potential future work is to understand the effects of recycled water on oil production from the well. An increase in oil production from recycled wells could help pay for the additional cost of treating the water for recycling. Additional quantitative data point that would be beneficial is produced water quantity. Both the oil and natural gas and the produced water production would assist in developing a cost model for the entire process of the well from fracturing through water collection, treatment and disposal.

A third potential research opportunity is to gain an understanding of the inorganic and metals differences and what those differences mean for the well and the produced water.

As recycling becomes more common and more wells are fractured using recycled water, the issues regarding this type of water management strategy will become clearer. Maintaining an inquisitive outlook regarding this process will be beneficial as new strategies and solutions might arise from continued inquisition into the process, especially considering the uncertainty around the mechanisms and pathways deep underground that affect the quality of the produced water. An inquisitive outlook will likely lead to more advanced research and data

acquisition. The data will allow oil and gas operators to make more informed data driven decisions to help effectively manage their business while improving their ability to recycle or beneficially reuse produced water. With an improved recycling program, operators can minimize their dependence on freshwater, lower their environmental footprint and benefit the society in which they operate.

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